

THERMODYNAMIC PROPERTIES OF SOME
LANTHANOID DICARBOXYLATE COMPLEXES

by

Ingemar Dellien


Lund 1973
 



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AVHANDLING FÖR FILOSOFIE DOKTORSEXAMEN

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Ingemar Dellien

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This dissertation consists of a review, summarizing the results from the following publications, numbered I-IV:

- I. Dellien, I. and Grenthe, I. Stability Constants for the Lanthanoid Malonate and Hydrogen Malonate Complexes. Acta Chem. Scand. 25 (1971) 1387.
- II. Dellien, I. Free Energy, Enthalpy and Entropy Changes for the Formation of Lanthanoid Malonate and Hydrogen Malonate Complexes. Acta Chem. Scand. In press.
- III. Dellien, I., Grenthe, I., and Hessler, G. Free Energy, Enthalpy and Entropy Changes for the Formation of Some Lanthanoid Thiodiacetate Complexes. Acta Chem. Scand. Submitted for publication.
- IV. Dellien, I., and Malmsten, L-Å. Free Energy, Enthalpy and Entropy Changes for the Formation of Some Lanthanoid Maleate Complexes. Acta Chem. Scand. Submitted for publication.

INTRODUCTION

The lanthanoids comprise the elements from number 57 lanthanum to number 71 lutetium. The configuration of the outer orbitals of these elements is $4f^n 5s^2 5p^6 5d^1 6s^2$, where n is zero for lanthanum and fourteen for lutetium. The same arrangement of the outer electrons gives similar properties to all elements of the series. The most important oxidation number is +3, and in solution they form complexes of approximately the same type and strength with a given ligand.

The coordination chemistry of the lanthanoids in solution has been extensively studied during the last decades. This work has been motivated both from a practical and a theoretical point of view.

The similar chemical properties of the lanthanoids makes the separation of them with such classical methods as fractional crystallization a difficult and time-consuming task. More efficient methods are provided by the use of ion-exchange resins or liquid-liquid extraction. Knowledge of the stability constants of various lanthanoid complexes is essential in this connexion as they enable the calculation of the optimal conditions for a certain separation process. Two different types of ligands have proved to be useful for this purpose, viz. hydroxo-carboxylates (e.g. α -hydroxy-isobutyrate) and aminopolycarboxylates (e.g. EDTA). A large number of stability constants of lanthanoid complexes with these types of ligands have been determined^{1,2}.

The increased nuclear charge from lanthanum to lutetium makes the size of the ions decrease monotonously across the lanthanoid series. As ligand field effects are an order of magnitude smaller for the lanthanoids than for the typical

d-transition elements, the lanthanoids provide an opportunity to study the effects of ionic size on chemical properties. Precise thermodynamic data for the formation of complex species in solution as well as structural studies of crystals containing the complexes are of interest from this more theoretical point of view.

The purpose of the present study.

Various thermodynamic properties of rare earth complexes in solution have been studied in a series of investigations performed at this institute³⁻²⁰. The free energy of complexation has been determined for a number of carboxylate ligands with conventional experimental methods such as potentiometry, solubility measurements and solvent-solvent extraction. Calorimetric determinations of the corresponding heats of complexation have been made for most of the systems studied. For this purpose, Grenthe, Ots and Ginstrup have constructed a titration calorimeter. The partial molar heat capacities have been determined for rare earth perchlorates and oxydiacetates¹⁹.

The main objects of this investigation are summarized below.

i. The composition, stability and enthalpy of formation of the various complexes formed between trivalent lanthanoid ions and the ligands malonate, maleate and thiodiacetate have been determined. The properties of at least five lanthanoid systems have been studied for each ligand. Thus, the main features in the variation of the free energy, enthalpy and entropy of complexation across the lanthanoid series have been determined.

The free energy changes have been calculated from the relationship

$$\underline{\Delta G}_j^{\circ} = -RT \cdot \ln \beta_j$$

The stability constants have been determined with a conventional potentiometric method, using hydrogen ion as competitor for the ligand and determining the concentration of free hydrogen ion with a glass electrode.

The enthalpy changes have been determined in a direct calorimetric procedure, using the calorimeter developed by Grenthe et al.¹⁴. The entropy changes are then obtained from the equation

$$\underline{\Delta G}_j^{\circ} = \underline{\Delta H}_j^{\circ} - T \cdot \underline{\Delta S}_j^{\circ}$$

ii. Some terdentate ligands with similar geometrical properties, viz. oxydiacetate⁶, iminodiacetate¹⁸ and dipicolinate⁴ have been studied earlier. These measurements have been extended to comprise the ligand thiodiacetate, which will permit a comparison between the donor properties of ether oxygen, thioether sulphur, imino nitrogen and aromatic nitrogen.

iii. The lanthanoid complexes with a series of dicarboxylate anions are suitable for a study of how the size of the chelate ring influences the thermodynamic quantities. The results of the calorimetric measurements will give information on whether changes in stability with ring size can be attributed to enthalpy or entropy effects.

iv. X-ray determinations of the structures of rare earth compounds demonstrate the importance of geometrical

factors for the properties of rare earth complexes. The structural investigation by Albertsson²¹ on tris(oxydiacetato)-lanthanoid(III) complexes indicated that the ligand-ligand repulsions increased with decreasing size of the central ion. These findings can be correlated with the fact that the stability in solution of the third lanthanoid-oxydiacetate complex decreases with decreasing central ion radius for the elements following erbium in the lanthanoid series.⁶ The lanthanoid-like Sc^{3+} -ion, which is smaller than the lanthanoids, does not form any third oxydiacetate complex at all in aqueous solution¹³.

The tris-oxydiacetato complexes exist as discrete units in the solid state and it is probable that this unit exists in solution as well, thus indicating a coordination number of nine in solution.

In some cases at least, it should be possible to find correlations between the properties of complexes in solution and the corresponding complexes in the solid state. Results from structural investigations on lanthanoid malonates²² and thiodiacetates²³ are available and work is in progress on some maleates²⁴.

v. The ligands used here are all anions of dicarboxylic acids. It has been shown that not only binary complexes of the type MA_j but also ternary complexes, generally $\text{M} \begin{smallmatrix} \text{H} & \text{A} \\ \text{p} & \text{q} & \text{r} \end{smallmatrix}$, are formed in these systems. This makes it harder both to choose a model to use in the calculations and to calculate the stability constants from the primary data. In some cases, it might even be impossible to make an unambiguous interpretation of the experimental data.

Some difficulties met with when choosing a model and in treating the data will be discussed.

Some aspects of the complex formation reactions of the lanthanoids in solution.

a. The variation of properties with the atomic number.

The lanthanoids are typical (a)²⁵ or "hard" acceptors, for which the bonding in a complex species is mainly of electrostatic nature. The influences of the 4f-electrons and of ligand field effects on the thermodynamic properties are of minor importance. The decreasing ion size on the other hand has a profound influence on the coordination chemistry of the various lanthanoid ions. This fact makes it interesting to investigate the variation of thermodynamic properties of various complexes across the lanthanoid series and to see whether these properties can be correlated with decreasing ionic radius. From an electrostatic point of view, the stability of a complex with a given charged ligand should be expected to increase with decreasing central ion size. However, it has long been known that the variation of stability constants etc. with ionic radius is not regular within the lanthanoid series. An example is given in Fig. 1, which shows the variation of ΔH_1^0 vs. Z for some terdentate ligands. Moeller² has discussed three major types of variation for the stability constants, namely (1) a more or less regular increase in stability with increasing atomic number; or an increase to gadolinium - dysprosium, followed by (2) constant stability or (3) a decrease in stability to lutetium.

The non-monotonic variation of the thermodynamic parameters

with the size of the central ion has been interpreted in three different ways, viz. (i) as due to changes in geometry or coordination number of the complex, or (ii) as due to changes in geometry or coordination number of the hydrated central ion, or (iii) as due to ligand field effects. Thus, the non-monotonic increase of complex stability with the atomic number found for the lanthanoid aminopolycarboxylates was described as due to a change in the number of donor groups utilized by the ligand when the metal ion radius decreased. For example, in the EDTA complexes the ligand might use six donor sites with the large cations and only five with the small ones²⁷. These arguments were based on the assumption that the coordination number of all the lanthanoids was equal to six, which is the typical coordination number for the 3d-transition elements. It is now generally accepted, that the lanthanoids have higher coordination numbers, often 8 or 9. The coordination number of the hydrated metal ions in solution has not been experimentally determined. Spedding et al.²⁸ made extensive studies of properties of solutions of simple inorganic lanthanoid salts. These properties, e.g. partial molar volumes, conductance, transference numbers etc., did not vary smoothly with the metal ion radius. A change in coordination number of the hydrated lanthanoid ion at a critical radius was postulated to account for this behaviour. These findings have repeatedly been invoked to account for the observed irregularities in the changes in free energy etc. for various complexation reactions.

The quantitative characterizations of this asserted change in hydration number are, however, somewhat contradictory. The change occurs "somewhere in the middle" of the series. This

vague expression is necessitated by the fact that the change occurs at different positions in the lanthanoid series, when different properties are studied.

From measurements of apparent partial molar volumes of lanthanoid trichlorides, Spedding et al. concluded that the hydration number changed from 9 for the elements La - Nd to 8 for the elements Gd - Lu²⁹. Using Speddings' data, Padova instead found an increase in hydration number to 11 for Dy³⁰. From the conductance data of Spedding et al., Choppin and Graffeo also found an increase in the hydration number, from about 13 for La to 14 for Lu³¹.

The results show that it is difficult to assign definite hydration numbers to these cations. This is partly due to the lack of any experimental procedure, which gives direct information on this property.

Geier et al.³² emphasized that the irregular variation of properties along the lanthanoid series need not necessarily be due to any change in coordination number of the hydrated metal ions. From spectrophotometric studies on lanthanoid-EDTA-complexes at different temperatures, they concluded that the hydration number was the same for all the lanthanoid ions, but that there exists an equilibrium of the type



for which the equilibrium constant is close to 1 in the middle of the series.

It was pointed out by Grenthe and Ots that heat capacity data can be used to study equilibria of the type (1)¹⁶. The presence of such equilibria for the species LnEDTA^- and $\text{Ln}(\text{oxydiacetate})_2^-$ has been established in this way^{17,20}. Additional support that the hydration equilibria occurred in

the complexes and not in the hydrated metal ions was obtained from partial molar heat capacity data for the lanthanoid perchlorates¹⁹, which gave no indication for the presence of any Z-dependent hydration equilibrium for the hydrated metal ions.

As a rule, it is not possible to make any unambiguous molecular interpretation of thermodynamic data on complexation reactions. This is partly due to the difficulty of deciding which particle (or particles) that is responsible for an observed change in a " Δ "-quantity. Such a decision could, however, be made for the changes in $\frac{\Delta C_p^0}{p}$, as the partial molar heat capacities could be determined for the reactants and the products. It is also as a rule not possible to determine the composition of the various species participating in a complexation reaction, with respect to medium ions and solvent molecules. Further, there is no model available for the description of electrolyte solutions which is capable of giving any quantitative estimates of thermodynamic properties of lanthanoid complexes in aqueous solution.

One way of getting a better understanding of thermodynamic data is to make correlations with other types of data, e.g. spectroscopic and kinetic. Of special interest in this connexion is the study of Reuben and Fiat on the ^{17}O chemical shifts, measured on various rare earth salts in aqueous solution at different concentrations and temperatures³³. They found a linear relationship between the shift and the total concentration of the rare earth salt within a wide concentration range. These findings indicate the absence of any hydration equilibria of the type (1) for the hydrated rare earth cations themselves.

The variation pattern of thermodynamic properties has also been regarded as due to ligand field effects, and at least one detailed attempt to correlate the change in stability constants in the lanthanoid series with ligand field effect stabilization has been made³⁴. Orbital interaction between the ligand and the 4f-electrons of the lanthanoid ions was postulated. However, there are spectral and thermodynamic evidences that such a stabilization is energetically small³⁵ (in the order of ≈ 1 kJ/mol). Hence, it will be difficult to establish the effect experimentally.

The position of yttrium is of interest in this connexion. The radius of the Y^{3+} -ion is 0.892 Å, which is about the same as for Ho^{3+} (0.894 Å). The stability constants of yttrium complexes have sometimes values which correspond to its ionic radius; in other cases the stability constants are near those of cerium or praseodymium. On the other hand, a comparison of the entropy values for the formation of yttrium complexes with the corresponding lanthanoid complexes shows that the values of ΔS_1^0 for yttrium complexes always correspond to a position between Dy^{3+} and Er^{3+} , i.e. the value expected from its ionic radius.

Hinchey and Cobble have pointed out that the entropy of formation for Ho^{3+} complexes would decrease with approximately $20 \text{ J.K}^{-1}.\text{mol}^{-1}$ if the degeneracy of the states for the 4f-electrons was removed as a result of complex formation³⁶. There is no such internal electronic entropy for Y^{3+} , which has no 4f-electrons. The similar ΔS_1^0 -values for the formation of Y^{3+} and Ho^{3+} complexes indicate that no change in the degeneracy of the 4f energy levels is obtained in the complexation reactions. This is another indication of the minor importance of ligand field effects for the thermodynamic stability of lanthanoid complexes.

b. Donor properties of different atoms.

The lanthanoids form, as a rule, rather weak complexes as compared to the typical transition elements. In keeping with the "hard acid" character of the lanthanoids, the most stable complexes are formed with ligands containing strongly electro-negative donor atoms such as nitrogen and oxygen. Many lanthanoid complexes with ligands containing oxygen donors have been investigated and characterized, both in solution and in the solid state. The stability of complexes with uncharged ligands containing nitrogen can not be studied in aqueous solution, as such ligands, e.g. aliphatic amines, are sufficiently basic to precipitate the metal hydroxides from water solution. However, Forsberg and Moeller have isolated complexes such as $[\text{Ln}(\text{en})_4](\text{NO}_3)_3$, $[\text{Ln}(\text{dien})_3](\text{NO}_3)_3$ and $[\text{Ln}(\text{dien})_2(\text{NO}_3)_2]\text{NO}_3$ (en = ethylenediamine, dien = diethylenetriamine) utilizing acetonitrile as the reaction medium^{37,38}. The cationic species possess a considerable thermodynamic stability in this solvent. The high stability is due to the favourable enthalpy of formation, whereas the entropy term is negative. Complexes with ligands containing aromatic nitrogen donors have been prepared from ethanolic solution, e.g. $[\text{Eu}(1,10\text{-phenanthroline})_2(\text{NO}_3)_2]\text{NO}_3$ and $[\text{Eu}(\text{bipyridyl})_2(\text{NO}_3)_2]\text{NO}_3$ ^{39,40}.

One way to get information on the donor properties of various atoms is to vary systematically the donors in series of related ligands, for which ligand specific geometric effects are small. Such geometric effects are more likely to appear in ligands with many donor groups and in the higher complexes formed with a given ligand. The terdentate ligands dipicolinate, iminodiacetate and oxydiacetate form complexes with quite different stabilities; differences which are

almost entirely due to an enthalpy effect. The variation in ΔH_1^0 for the various ligands through the rare earth series is very nearly the same (Fig. 1). It is reasonable to conclude that there are no ligand specific geometrical effects which influence the variation of thermodynamic quantities through the lanthanoid series for this series of ligands. This means that the differences in stability for these ligands can be ascribed to the decrease in donor properties in the series aromatic nitrogen > aliphatic nitrogen $\geq$ ether oxygen. These findings are in qualitative agreement with the fact that ethylenediamine-N,N'-diacetate (EDDA) forms more stable complexes than the corresponding ligand with only oxygen donors, viz. ethylene-bisglycolate^{41,42}.

The data available for ligands containing sulphur are sparse. The low stability of the 1,2-bis(carboxymethylthio)ethane (ETG) complex with Sm^{3+} ($\beta_1 \approx 200 \text{ M}^{-1}$)⁴² gives further evidence that sulphur is a poor donor to lanthanoid ions. This finding is in concordance with Choppin's and Martinez-Perez' interpretation of their results on the formation of α - and β -mercaptopropionates⁴³.

c. Effects of the size of the chelate ring.

The effect of the chelate ring size on the stability of complexes has been studied by Nancollas et al.⁴⁴⁻⁴⁶ for the complexes of the transition metal ions Mn^{2+} , Co^{2+} and Ni^{2+} with the ligands oxalate, malonate and succinate. These ligands form complexes with 5, 6 and 7 atoms in the chelate ring, respectively. A regular decrease in stability with increasing ring size was found for the first complex. The enthalpy of formation followed the order succinate > malonate > oxalate, whereas the entropy term followed the order malonate > oxalate > succinate.

d. Coordination in the solid state.

Determinations of crystal structures with X-ray diffraction and other methods have shown that the lanthanoid ions tend to form complexes with high coordination numbers, varying from six to twelve. The presence of octahedral lanthanoid(III)-complexes has been demonstrated in the halides, prepared under anhydrous conditions⁴⁷. Twelve-coordination has been established in the compound $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, where six nitrate ions act as bidentate ligands to the Ce^{3+} -ion⁴⁸. Coordination numbers eight and nine are common for the chelate complexes formed with bidentate and tridentate carboxylate ligands.

The structural effects of the decreasing ionic size with increasing Z have been elucidated from some crystallographic investigations on series of analogous compounds. Albertsson has studied the nine-coordinated tris(oxydiacetato)- and tris(dipicolinato)-lanthanoid compounds through the lanthanoid series⁴⁹. The coordination polyhedra were in all cases described as distorted versions of a symmetrically tri-capped trigonal prism. There is a decrease in the unit cell volume with decreasing cation radius. For the light lanthanoids (La - Gd), this volume decrease is only slightly less than expected from the decrease in central ion radius, but for the heavy lanthanoids the unit cell contraction is appreciably smaller than the metal ion radius decrease. This finding was considered to be a result of increasing repulsions between the coordinated oxygen donors, when the complex is contracted. The coordination number is, however, the same throughout the lanthanoid series. The consistency of these structural data with the interpretation by Grenthe et al. of thermodynamic data for the formation of the corresponding complexes in solution has already been mentioned (p. 6.).

Some geometrical effects of exchanging the ether oxygen in oxydiacetate for sulphur in thiodiacetate have been found in the solid state for the compounds $\text{Na}_3[\text{Nd}(\text{oxydiacetate})_3] \cdot 2\text{NaClO}_4 \cdot 6\text{H}_2\text{O}$ ²¹ and $[\text{Nd}(\text{thiodiacetate})(\text{H}_2\text{O})_3] \cdot \text{Cl}$ ²³. The coordination polyhedron around neodymium can in both cases be described as a trigonal prism. The thiodiacetate ion is not planar in the complex as in the case of the oxydiacetate, but coordinates with two carboxylate oxygens in adjacent corners of a rectangular face of the prism, while the sulphur atom is "bent out", occupying a position outside the rectangular face. This distortion can be correlated with the larger radius of the sulphur atom as compared to oxygen. The $\text{Nd}^{3+} - \text{COO}^-$ -distances would be too long with a planar thiodiacetate ligand. As the bond lengths within the ligand can not be changed very much, reasonable bonding distances are obtained by a change of conformation of the ligand. The distance between the two coordinated carboxylate oxygen atoms is very short, 3.1 Å, whereas the $\text{Nd}^{3+} - \text{S}$ -distance is 3.15 Å, a value somewhat larger than the sum of the van der Waals radii of these atoms.

It is not possible to correlate the low stability of the third lanthanoid thiodiacetate complex in solution, if this complex is formed at all, with structural data as has been done for the oxydiacetates. It is, however, reasonable to assume that the larger sulphur atom will enhance the steric hindrance effect found for the formation of the third oxydiacetate complexes with the smallest lanthanoids.

The importance of repulsions between coordinated oxygen atoms in deciding the geometry and stability of solid rare earth complexes has also been demonstrated for the glycolato^{50,51},

oxalato⁵² and malonato²² complexes. These bidentate ligands form nine-coordinated complexes with the light lanthanoids, but there is a change in structure, including a lowering of the coordination number to eight, when the metal ion radius decreases. This change occurs around Gd for the glycolates, around Ho-Er for the oxalates and around Eu-Gd for the malonates. The average O-O distances are larger in an eight-coordinated complex than in a nine-coordinated, presumably resulting in smaller ligand-ligand repulsive forces.

The decrease in coordination number in these complexes can be described as a result of the larger freedom possessed by the bidentate as compared to the terdentate ligands in the formation of a coordination polyhedron. One also finds larger distortions of the coordination polyhedra from the idealized ground geometries for the bidentate ligands.

EXPERIMENTAL.

All thermodynamic quantities determined in these investigations refer to a temperature of 25.0 °C and an aqueous sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M. This choice of medium is of advantage in the calorimetric measurements, as it makes corrections for the heat of dilution of the sodium ion unnecessary. Such corrections would otherwise have been large.

The equilibrium constants have been calculated under the assumption that the variation of the activity factors of the various species is negligible when the composition of the solutions is changed. The ligands studied here form rather weak complexes with the lanthanoids, which means that considerable amounts of the perchlorate ions must be exchanged for the ligand ions in the measurements. The ionic strength is thus not constant but varies with at most 10 per cent. Since activity factors as a rule do not vary very much with ionic strength at ionic strengths around 1 M, it is believed that no serious errors are introduced by this variation.

A medium with a higher ionic strength, say 3 M, would have made the relative changes in ionic strength smaller. Also, possible diffusion potentials would be diminished (vide infra). However, it would be difficult to compare the results obtained from such experimental conditions with earlier data, as very few investigations have been performed at such a high ionic strength.

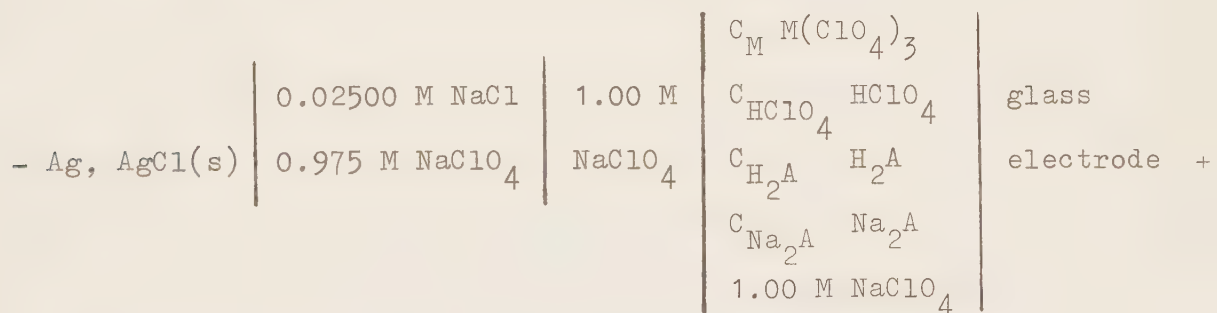
The possible existence of a third thiodiacetate complex, MA_3^{3-} , was investigated in 4 M NaClO_4 . As this complex is weak, if it is formed at all, it is necessary to get accurate experi-

mental data at high concentrations of free ligand. The high concentration of the ionic medium was chosen in order to minimize ionic strength variations and diffusion potentials (part III₄).

The solutions used have been prepared and standardized with conventional methods (part I). One difficulty met with is the determination of the excess of perchloric acid in the metal perchlorate stock solutions. This has been done potentiometrically, but the reproducibility was low in a few cases and amounted to ± 2 mV. This lowers the precision of the first points ($\bar{n} < 0.1$) in a potentiometric titration series.

Potentiometric measurements.

There are no electrodes available for a direct determination of the concentration of free metal ion or ligand in the systems investigated here. Instead, the competition between hydrogen ion and metal ion for the ligand has been utilized. The hydrogen ion concentration is determined from emf measurements on galvanic cells of the type:



The system is calibrated by measuring the emf when the right half-cell contains a solution with known hydrogen ion concentration (10.00 mM HClO₄).

The emf of the galvanic cell used can be written as

$\underline{E}/\text{mV} = \underline{E}_0/\text{mV} + 59.16 \cdot \log(\underline{h}/M) + \underline{E}_j/\text{mV}$, where $\underline{h}$ is the hydrogen ion concentration and $\underline{E}_j$ is the liquid junction potential. From the measurements on the proton-malonate system, the liquid junction potential was found to be the sum of two terms, $\underline{E}_j = \underline{E}_{\underline{h},j} + \underline{E}_{\underline{a},j}$, where $\underline{E}_{\underline{h},j}$ is the hydrogen-ion dependent liquid junction potential and $\underline{E}_{\underline{a},j}$ is the liquid junction potential dependent on the difference in perchlorate ion concentration between the half-cells (part I, p. 1393). A constant value of the protonation constant, $\beta_{0,1,1}$, was obtained for $\underline{C}_A$ -values up to 100 mM, when the measured emf-values were corrected for the liquid junction potential, $\underline{E}_j$. The same value of the protonation constant was obtained when the measurements were repeated in a diffusion-free cell.

The formal description of the increase in $\beta_{0,1,1}$ with $\underline{C}_A$ as due to an uncompensated liquid junction potential is supported by these findings, which also indicate that the effects caused by the differences in ionic medium in the various titrations are small.

Similar effects were found in the proton-maleate system. The emf-data on the various maleate systems have thus been corrected for this liquid junction potential.

$\underline{E}_{\underline{a},j}$ is a linear function of the difference in perchlorate ion concentration between the half-cells and the slope was found to be -7.8 mV/M in the malonate system and -6.4 mV/M in the maleate system.

Calorimetric measurements.

The calorimetric equipment used has been described in detail by Grenthe, Ots and Ginstrup¹⁴.

The measurements were performed as titrations, which allows a large number of experimental points to be determined in a comparatively short time. The description given in part II for the malonate system is valid for the maleates and thiodiacetates as well. Ahrlund and Kullberg have used the same technique and the same calorimeter⁵³.

CALCULATIONS

With the experimental procedure used here, the composition and stability of the various complexes formed have to be calculated from $(\underline{C}_M, \underline{C}_H, \underline{C}_A, \underline{h})$ - data. One approach is to calculate formation curves, $\bar{n}(\underline{a})$, assuming that only species of the type $MA_{\underline{j}}$ are formed. The correctness of this assumption is then checked by making variations of the experimental conditions. Thus, if the formation curves are independent of $\underline{C}_M$, it might be concluded that polynuclear species are not formed in appreciable amounts. When the ligand, A, is the conjugate base of a polyprotic acid, it must be ascertained whether protonated species also act as ligands. A variation of the formation curves with the ratio $\underline{C}_H/\underline{C}_A$ indicates the formation of species of the type $MH_{\underline{q}}A_{\underline{r}}$ with $q \geq 1$.

When polynuclear or acid complexes are formed in a system, the $\bar{n}(\underline{a})$ - curves are calculated from erroneous assumptions. Some properties of such "false" formation curves have been discussed in part I.

In the malonate and thiodiacetate systems the calculated $\bar{n}$ vs. $\underline{a}$ curves were clearly functions of $\underline{C}_H/\underline{C}_A$ but not of $\underline{C}_M$, indicating that species of the type $MH_{\underline{q}}A_{\underline{r}}$ with $q \geq 1$ were formed. The calculations are rather cumbersome in such systems. It is, for example not always possible to calculate the concentration of free ligand, $\underline{a}$, without making assumptions regarding the composition and stability of the mixed complex(es) formed.

Some graphical procedures have been devised to solve such problems, and the method described by Österberg⁵⁴ has been

tried on a malonate system. The composition and stability of the species present can be obtained via a graphical determination of the free ligand concentration in the solutions. The method is applicable when precise measurements can be made in solutions, where the concentration of metal complexes is small compared with that of the proton-ligand complexes. This was not feasible for the malonates. An iterative procedure also failed, probably because Österberg's method is sensitive to an error in the starting value, $\underline{a}_0$, for the concentration of free ligand.

Instead, all data have been analyzed with the least-squares procedure "LETAGROP", developed by Sillén and co-workers^{55,56}. The calculations have mainly been made with the Univac 1108 computer in Lund.

In these calculations one has to assume a certain set of complexes and estimates of their stability constants. This model is then refined until the best agreement with the experimental data is obtained. The $\bar{n}^*(\underline{a}^*)$ -formation curves, which can be calculated directly from the experimental data, have been used to obtain information on which binary complexes MA_j that were formed and to get preliminary estimates of the corresponding stability constants. The variation of the $\bar{n}^*(\underline{a}^*)$ -curves with $\underline{C}_H/\underline{C}_A$ was assumed to be caused by an acid complex with the composition MHA, for which the stability constant was estimated from the corresponding acetate system. $\underline{C}_H/\underline{C}_A$ has been used as the error-carrying variable.

The error in $\underline{C}_H/\underline{C}_A$ increased with increasing free ligand concentration. These systematic differences indicated that the first model had to be modified. If a complex MHA_2 was included

in the model, the standard deviation in $\frac{C_H}{C_A}$ decreased with a factor 2.

Models containing other complexes, binuclear as M_2A and ternary as MH_2A and MH_2A_2 , were also tried. However, the standard deviation did not decrease substantially, and the corresponding stability constants were not significantly positive. Hence, there is no evidence for the formation of any species of this type in these systems.

The interpretation of the experimental data for the maleate systems has been discussed in part IV.

The final values of the standard deviation in $\frac{C_H}{C_A}$, $\text{sig}(\frac{C_H}{C_A})$, are in the range $3 \cdot 10^{-3}$ - $10 \cdot 10^{-3}$. It is not easy to determine directly whether these values correspond to a reasonable agreement of the experimental and the calculated $\frac{C_H}{C_A}$ -values. However, such an estimate must be made in order to decide whether an observed decrease in $\text{sig}(\frac{C_H}{C_A})$ is experimentally significant or not. The value of $\text{sig}(\frac{C_H}{C_A})$, for example, decreases from $3.8 \cdot 10^{-3}$ to $3.3 \cdot 10^{-3}$ in the Pr-maleate system when the acid complex MHA is introduced (part IV, Table 3). It was shown that this difference in $\text{sig}(\frac{C_H}{C_A})$ was not significant when the experimental errors were taken into account. The standard deviation decreases from $7.8 \cdot 10^{-3}$ to $4.5 \cdot 10^{-3}$ in the Tb-thiodiacetate system when MHA_2 is included in the calculations. This decrease has been considered to be significant and the final model for the thiodiacetates includes the complex MHA_2 .

In order to get an estimate of what could be regarded as reasonable values of $\text{sig}(\frac{C_H}{C_A})$, some calculations have been performed for the Pr-maleate system in the following way. The

measured emf-values were adjusted to give an exact fit with the final constants (part IV, Table 2) and the total concentrations in the solutions (Table 1). Reasonable "random errors" were then added to the values of the concentrations, initial volume and emf (the mean error in $\underline{E}$ was estimated to 0.1 mV, in $\underline{C}_H$ to 0.15 %, etc). The "best" constants and $\underline{\text{sig}}(\underline{C}_H/\underline{C}_A)$ were calculated. Values of $\underline{\text{sig}}(\underline{C}_H/\underline{C}_A)$ in the range $3 \cdot 10^{-3}$ - $7 \cdot 10^{-3}$ were obtained, which shows that the chemical models used describe the experimental data satisfactorily.

The weighting scheme, which gives all experimental points equal weight, can be questioned. The first few points in a titration series have uncertain values of $\underline{C}_H/\underline{C}_A$, due to the difficulty of determining the excess of perchloric acid in the metal stock solutions (cf. p. 18). As these points have high $\underline{C}_H/\underline{C}_A$ -values, the error square sum $\underline{U}$ depends strongly on these points. It has in some cases been possible to lower $\underline{U}$ and thus $\underline{\text{sig}}(\underline{C}_H/\underline{C}_A)$ considerably by a small adjustment of $\underline{C}_{H,S}$.

Approximately the same stability constants are obtained when different least-squares procedures are applied (part IV, Tables 2 and 3). Some protonation constants and formation constants for maleate systems have also been calculated with standard graphical methods, and the results were the same as those obtained from the least-squares calculations.

An incorrect weighting scheme can be expected to give erroneous estimates of the standard deviations of the constants. In order to get information on the magnitude of such effects, both $\underline{C}_H/\underline{C}_A$ and $\underline{E}$ were used as the error-carrying variable in some maleate systems (part IV, Table 3).

The use of $\underline{E}$ instead of $\underline{C}_H/\underline{C}_A$ as the error-carrying variable lowers the estimates of the standard deviations of the constants. The differences are small for the constants $\beta_{1,0,\underline{j}}$, but unrealistically small errors were calculated for the constant $\beta_{1,1,1}$. However, these very time-consuming calculations were not brought to completion ("GAMLA KONSTANTER") which may be a reason for these findings, besides an inappropriate weighting.

It is desirable to use both graphical and numerical methods (i.e. least-squares methods) in the determination of stability constants. This is true especially for the type of systems investigated here, where the primary data do not give any direct information on what kind of species that are present. The constants finally obtained from the computer calculations have been used to calculate a set of curves, $\bar{n}^*(\underline{a}^*)$, which, even if they strictly speaking have no direct chemical meaning, give an idea of how good the calculated constants describe the experimental points. The calculated $\bar{n}^*(\underline{a}^*)$ -curves shown in Fig. 1, part III, describe the experimental points satisfactorily.

The effect of excluding the complex MHA_2 in the calculations on the terbium thiodiacetate system was determined. If MHA is the only acid complex included in the calculations, $\text{sig}(\underline{C}_H/\underline{C}_A)$ becomes $7.75 \cdot 10^{-3}$, but it is lowered to $4.48 \cdot 10^{-3}$ when MHA_2 is included.

The difference between these two models is now known in terms of $\text{sig}(\underline{C}_H/\underline{C}_A)$ -values. In order to find out how this difference appears in a graphical treatment, the following procedure was used.⁵⁷ Let the functions $\underline{p}$ and $\underline{q}$ be defined as

$$\underline{p} = (\underline{C}_M - \sum_0^2 [\underline{MA}_n]) / (\underline{C}_M - \sum_1^2 [\underline{MA}_n])$$

and

$$\underline{q} = \sum_1^2 \underline{n} [\underline{MA}_n] / \sum_0^2 [\underline{MA}_n]$$

$\underline{q}$ is a function of $[A]$ only, and if $\beta_{1,1,2}$ is zero, then $\underline{p}$ is a function of $[HA]$ only. In this case, then (i) the functions $\underline{p}([HA])$ and $\underline{q}([A])$, respectively, should coincide for titration series with different compositions, and (ii) the function $\underline{p}/((1-\underline{p})[HA])$ vs. $[A]$ should be constant, independent of $[A]$. Figures 2 and 3a show that (i) holds "well", but $\underline{p}/((1-\underline{p})[HA])$ is not quite constant. This function has also been calculated with the final constants, including $\beta_{1,1,2}$, and Figure 3b shows a linear function of $[A]$. The deviations are somewhat smaller than in Figure 3a. It is clear that this method is not very good, if one wants to get an estimate of how much the description of the data is improved when the complex MHA_2 is included.

The set of "best" constants are calculated in the "LETA-GROP" programme from the minimum of the error-square sum $\underline{U}$, where $\underline{U}$ is a function of the various stability constants. The possibility of "local minima" in the $\underline{U}$ -surface has been discussed. The starting values of the parameters to be calculated must be chosen with care if such local minima are present. Otherwise the calculations might converge to the wrong minimum point.

When $\underline{C}_H/\underline{C}_A$ was used as the error-carrying variable, the calculations have always converged to the same point, even when quite erroneous initial guesses have been chosen deliberately. On the other hand, the use of the emf $\underline{E}$ as the error-carrying variable (part IV) requires good initial estimates

(within say 10 per cent), if excessive computing time for convergence is to be avoided.

The results of the calorimetric measurements have been calculated with the programme "LETAGROP KALLE"⁵⁸, which minimizes the error-square sum $\underline{U}$, defined as $\underline{U} = \sum_i (\underline{Q}_{i,\text{calc}} - \underline{Q}_{i,\text{exp}})^2$, where the summation is made over all experimental points "i". As $\underline{Q}_{\text{calc}}$ is a linear function of the $\underline{\Delta H}_i^0$ -values, the minimum value of $\underline{U}$ can be calculated directly, and no iterative procedure is necessary. The equal weighting of the experimental points seems to be a correct weighting scheme in this type of measurement. Graphical evaluation of the enthalpy values and their maximum errors gives approximately the same values as those obtained from the computer, given in parts II - IV.

DISCUSSION

The problems in establishing the composition and stability of the various complexes formed in these systems have been discussed in parts I-IV and in this review, p. 21.

The stability of the thiodiacetato complexes is low compared with the complexes formed with the other terdentate ligands discussed (oxydiacetate etc). Figure 1 shows that the variation pattern in ΔH_1^0 vs. Z is the same for the thiodiacetates as for the other ligands. It follows from the arguments presented previously (p. 13) that the low stability of the thiodiacetates can be referred to the poor donor ability of sulphur in this case.

The irregular variation of ΔH_1^0 across the lanthanoid series for the terdentate and other ligands (e.g. EDTA) may be compared with the corresponding functions for the bidentate ligands malonate and maleate. The variation within the series is "regular" and an approximately linear function of the size of the central ion (part II, Fig. 2b) for these ligands. This is also the case for some other bidentate ligands such as tropolonate⁵⁹, acetylacetonate⁶⁰ and kojate⁶¹.

The pattern shown in Figure 1 represents the "normal" trend, which has been interpreted as reflecting changes in the state of hydration of the metal ions across the lanthanoid series. With this description of the "normal" pattern, the behaviour of ΔH_1^0 vs. Z for the bidentate ligands has been interpreted as being due to the presence of several mono-ligand species of different hydration in equilibrium^{59,61}. The idea of variable hydration numbers for the lanthanoid ions is at variance with some experimental findings and also makes it difficult to

understand the regular pattern found for the bidentate ligands.

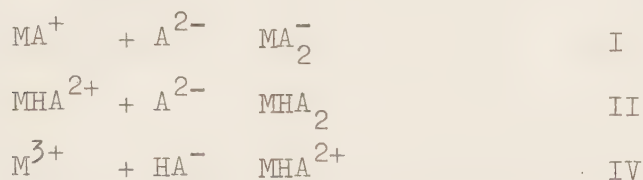
It is probably an over-simplification to attribute the non-monotonic variation of ΔH_1^0 , for example, to one common cause. The presence of a hydration equilibrium for the lanthanoid-EDTA and for the second lanthanoid oxydiacetate complexes has been established by spectrophotometric and thermodynamic methods.

In the mono-oxydiacetato complexes, no hydration equilibrium seems to be present in spite of the similar variation in ΔH_1^0 and ΔH_2^0 vs. Z for these complexes¹⁷. In addition to changes in geometry of the complexes, there might also be a change in the state of hydration of the metal ion; not necessarily a change in the number of coordinated water molecules but a change in geometry, brought about by the changing ionic radius.

The bidentate ligands have a larger freedom as compared to terdentate ligands in the formation of the coordination polyhedron (p. 16). It is possible that such geometrical effects may influence the thermodynamic properties of the complexes in solution, but it is not possible to make any correlations of the structural findings with the trends observed in ΔH_1^0 vs. Z for these ligands.

The entropy change for complexation reactions of the type discussed here is often regarded as due to the release of water molecules from the reactants in the association reaction. The discussion of the results from the malonate system (part II, p. 9) can be extended to the maleates and thiodiacetates. These systems show the same decrease in the order $\Delta S_1^0 > \Delta S_2^0$ for the stepwise entropy changes as found for the malonates and several other complexes.

Since complexes with the same stoichiometry are formed in the malonate and thiodiacetate systems, it is possible to compare the reactions



The same results are obtained for both systems, *i.e.* $\Delta S_{\text{II}}^{\circ} > \Delta S_{\text{I}}^{\circ}$ and $\Delta S_{\text{I}}^{\circ} > \Delta S_{\text{IV}}^{\circ}$. This last relationship is worth mentioning, as it indicates that thiodiacetate ion acts as a bidentate ligand when the second complex is formed. This conclusion is supported by the values of the ratio K_1/K_2 of the stepwise stability constants, which have values of the same order of magnitude for the thiodiacetates and the oxydiacetates. The geometrical constraints imposed by the presence of the bulky sulphur atom are thus noticeable only in the difficulty to form a third thiodiacetate complex.

The relationship $\Delta S_{\text{I}}^{\circ} > \Delta S_{\text{IV}}^{\circ}$ was also used to establish the bidentate character of the malonate ion. However, a strong chelating tendency for the malonate ion should make the acid MHA rather strong, whereas pK_{a} for MHA is about the same as for malonic acid itself. Thus, it was proposed that the chelating tendency of the malonate ion is weak (part I, p. 1399).

No definite conclusions concerning the chelating tendency of malonate ion can be drawn from this qualitative reasoning. It is an interesting finding that there are both chelating and non-chelating malonate ions in solid lanthanoid(III)malonate compounds²².

The malonate complexes may be compared with the corresponding oxalates¹², for which the high stability and the absence of acid complexes clearly indicates that oxalate ion predominantly forms a chelate in solution. This is in keeping with the fact that

only chelating oxalate ions are found in solid rare earth oxalate complexes⁵².

It has been established that the stability constants decrease in the order oxalates > malonates > maleates, which is the expected order when the chelate ring size increases. The enthalpy term is of about the same magnitude for the formation of malonate and maleate complexes, whereas the entropy term is more positive for the formation of malonate complexes. These data are in rough agreement with the results found for the formation of 3d-transition metal complexes (p. 14).

It is difficult to assess the effects on the stability of maleate complexes caused by the rigid geometry of this ligand. Structural investigations on solid rare earth maleates indicate that no geometrical constraints seem to be present for the formation of a chelate, *i.e.* the ligand "bite" is large enough to accommodate a lanthanoid ion²⁴.

The results presented here for the malonate and maleate systems can be compared with the investigations made by Choppin *et al.*^{62,63} and Roulet *et al.*⁶⁴ at ionic strength 0.10 M (NaClO_4).

An increase in $-\Delta G_1^0$ of about 5 kJ/mol is found both for the malonates and the maleates, when the ionic strength is lowered from 1 M to 0.1 M. The variation patterns of ΔG_1^0 vs. Z are thus not affected by the change in ionic strength.

The variation pattern in ΔH_1^0 vs. Z is the same at ionic strength 0.1 M and 1 M only for the maleates. The enthalpy change is more endothermic by about 2 kJ/mol at the lower ionic strength. The higher stability in 0.1 M NaClO_4 is thus due to the more favourable entropy change.

For the malonates at ionic strength 1 M, ΔH_1^0 increased with 2.6 kJ/mol and ΔS_1^0 with 24 J·K⁻¹·mol⁻¹ from lanthanum to lutetium (part II). Choppin et al. have found a decrease in ΔH_1^0 of 2.6 kJ/mol and a small increase in ΔS_1^0 of about 8 J·K⁻¹·mol⁻¹.

The qualitative disagreement between the results of these two investigations of the malonate system may partly be due to the fact that different models have been used. Degischer and Choppin found evidence for the formation of the complexas MA and MA₂, while also the presence of the complexes MA₃, MHA and MHA₂ has been taken into account when the enthalpy values valid in 1 M Na(ClO₄) were calculated.

The formation of the complexes MA and MA₂ in the maleate systems was established both by Roulet et al. and by the present author.

Attempts to find correlations between the basicity of the ligand and the complex stability have not been very successful. The complexes formed with the ligands oxalate, malonate and maleate may be quoted as an example. The strength of the proton complexes increases along the series ($\beta_{0,1,1} = 3.6 \cdot 10^3 \text{ M}^{-1}$, $1.2 \cdot 10^5 \text{ M}^{-1}$ and $4.2 \cdot 10^5 \text{ M}^{-1}$, respectively) whereas the stability of the lanthanoid complexes decreases ($\beta_{1,0,1} = 10^5 \text{ M}^{-1}$, $5 \cdot 10^3 \text{ M}^{-1}$ and $8 \cdot 10^2 \text{ M}^{-1}$, respectively).

The stabilities of the various acid lanthanoid complexes have some interesting features. Stability constants for the formation of the hydrogen malonate, hydrogen thiodiacetate and hydrogen ETG complex with Sm³⁺ have been determined. These ligands do not have the same basicity ($\log \frac{K_{H,HA}}{K_{H,HA}}$ is 2.58 for malonate and 3.26 for ETG⁴²) but the stability of the Sm³⁺ complex with these

ligands is very nearly the same, $\log K_{\text{Sm,HA}}$ is 1.53, 1.60 and 1.54, respectively. This finding illustrates the lack of correlation between the strength of the proton and lanthanoid complexes, respectively, for the formation of acid complexes (cf. part IV, Table 5).

A simple electrostatic model was applied when the stability of acid complexes was discussed in parts II and III. The acid strength of an acid complex is thus expected to decrease with increasing distance between the basic carboxylate groups. This distance increases considerably in the series malonate < thiodiacetate < ETG. The pK_{a} -values for the corresponding acid Sm^{3+} -complexes are 2.92, 2.69 and 3.08, respectively, in disagreement with the order expected from the ligand geometry.

Another striking feature is the strong variation of the pK_{a} -values across the lanthanoid series in some systems, viz. malonate, EDDA and IMDA. A decrease in pK_{a} with approximately 1 unit is observed when going from lanthanum to lutetium. The hydrogen thiodiacetates do not show this behaviour; pK_{a} is constant for the elements investigated.

The simple model used seems to be too crude to permit any detailed discussion of the properties of acid complexes. Structural data for acid lanthanoid complexes would be of value in this connexion.

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FIGURES

Figure 1. Plots of ΔH_1^0 vs. Z for the formation of lanthanoid thiodiacetate, oxydiacetate, iminodiacetate and dipicolinate complexes. The various curves have been drawn to give the best fit with the curve for the thiodiacetates.

Figure 2. q vs. $-\log([A]/M)$ and p vs. $-\log([HA]/M)$, respectively. (q and p are defined on p. 26). The curves have been calculated with data from the Tb-thiodiacetate system, assuming that $\beta_{1,1,2}$ is zero. Data from four different titration series have been used. The various symbols refer to series with the following compositions of the solutions.

o Series 1, Table 1 in part III.

Δ Series 2, Table 1 in part III.

S: $\underline{C}_H = 0.1007$ M, $\underline{C}_M = 0.01988$ M, $\underline{C}_A = 0.05013$ M;

$\square$ T: $\underline{C}_H = 0.00064$ M, $\underline{C}_M = 0.01990$ M, $\underline{C}_A = 0.05018$ M;

S: $\underline{C}_H = 0.00064$ M, $\underline{C}_M = 0.01990$ M, $\underline{C}_A = 0.05018$ M;

$\diamond$ T: $\underline{C}_H = 0.1007$ M, $\underline{C}_M = 0.01988$ M, $\underline{C}_A = 0.05013$ M;

Figure 3. $p/((1-p) \cdot [HA])$ vs. $[A]$, calculated

a. with $\beta_{1,1,2} = 0$,

b. with $\beta_{1,1,2} = 1.98 \cdot 10^7 \text{ M}^{-3}$.

The symbols have the same meaning as in Figure 2.

$\Delta H_f^\circ \text{ kJ/mol}$

Fig.1.

Ligand $\text{OOC}\cdot\text{R}\cdot\text{COO}$

$\text{R}=\text{CH}_2\cdot\text{S}\cdot\text{CH}_2$ $\square$ $a=0$

$\text{R}=\text{CH}_2\cdot\text{O}\cdot\text{CH}_2$ $\circ$ $a=-15$

$\text{R}=\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2$ $\triangle$ $a=-15.6$

$\text{R}=\text{C}_6\text{H}_5$ $\times$ $a=-29$

I estimated error

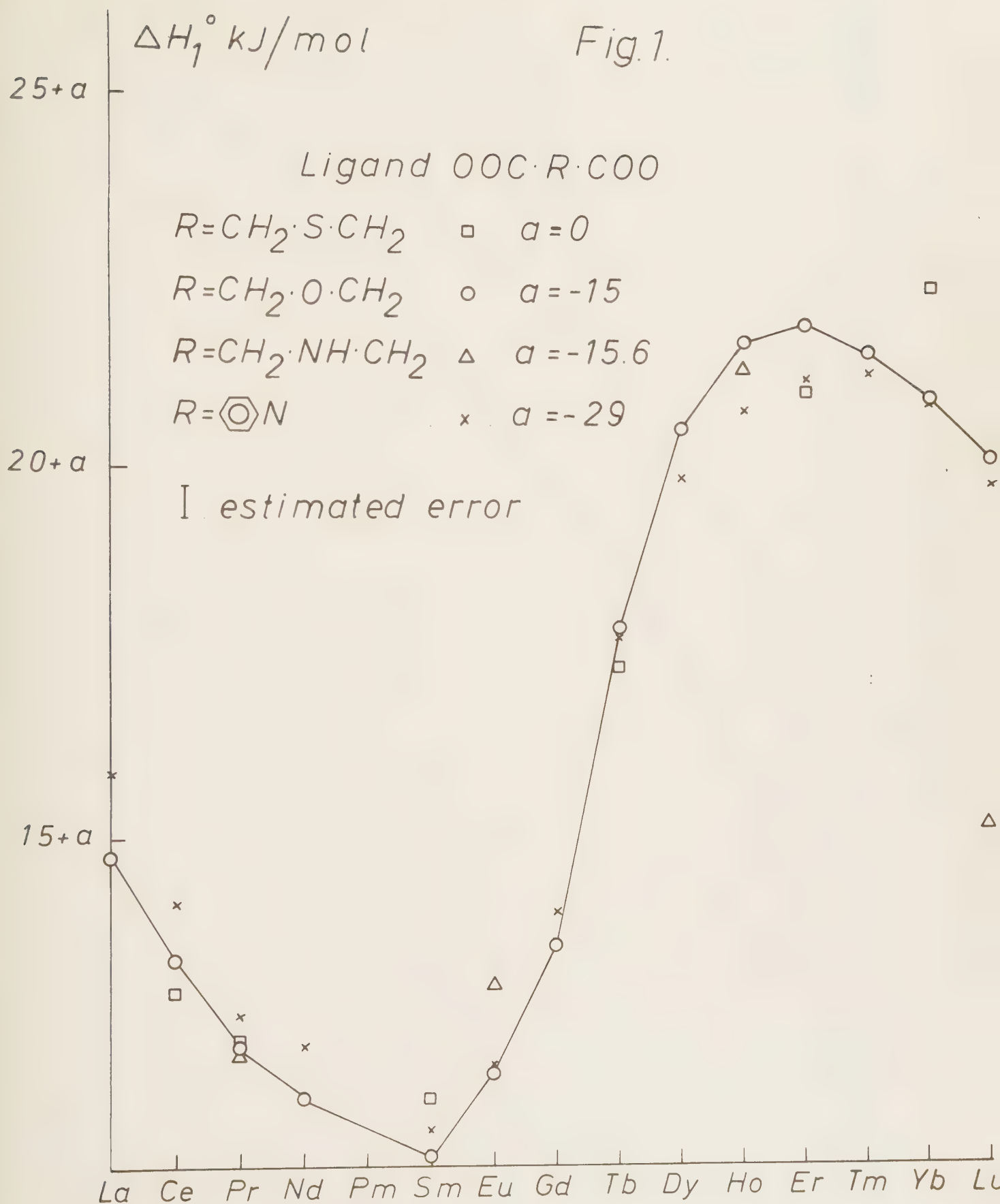
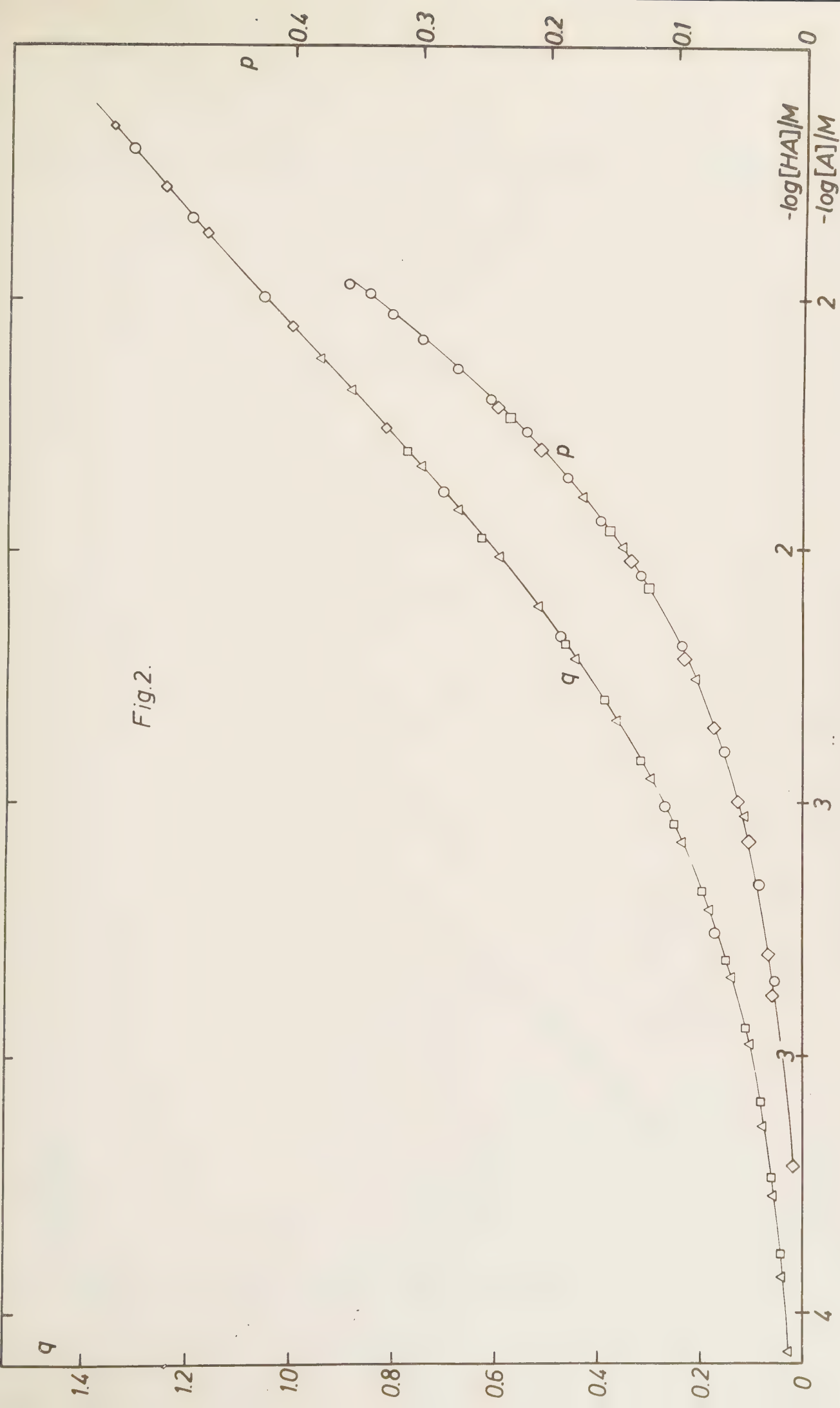


Fig.2.



$$\frac{P}{(1-p)[HA]} \cdot M$$

Fig. 3.



Part I.

Thermodynamic Properties of Rare Earth Complexes

IX. Stability Constants for the Lanthanoid Malonate and Hydrogen Malonate Complexes

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The stability constants for the formation of lanthanoid(III) malonate and bimalonate complexes of the compositions MA , MA_2 , MA_3 , MHA , and MHA_2 have been determined. All data refer to a temperature of 25.0°C and a sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M. The various systems were investigated by determining the concentration of free hydrogen ion by means of a glass electrode. Stability constants were obtained from the experimental data by a least-squares method ("Letagrop Vrid").

Thermodynamic studies of the complexes formed between the trivalent rare earths and a number of dicarboxylates have been reported in the previous parts of this series.¹⁻⁸ These studies have been extended to include the ligands malonate, maleate, thiodiacetate, and iminodiacetate. All ligands are potential chelating agents containing two carboxylate groups. The size of the chelate ring, if formed, varies from five atoms in oxalate to six in malonate, and seven in maleate.

Oxydiacetate, thiodiacetate, iminodiacetate, and 2,6-pyridine dicarboxylate are potential three-dentate ligands, where one donor atom is an ether oxygen, an ether sulfur, an aliphatic and an aromatic nitrogen, respectively. The various ligands have been chosen in this way in order to permit a discussion of the following points.

a. How are the stability constants influenced by the third donor atom in the three-dentate ligands and by the size of the chelate ring?

b. One expects a correlation between the stability of the chelate complex and the tendency to form acid or polynuclear complexes — the weaker the chelate the stronger the tendency for formation of mixed complexes. The occurrence of effects of this type may be studied as a function of the distance between the donor atoms in the series oxalate — malonate —

maleate and as a function of the donor atoms in the series dipicolinate — oxydiacetate — thiodiacetate.

c. The rare earth elements presumably have coordination numbers larger than six in aqueous solution. An estimate of the coordination number is obtained from the maximum number of ligands coordinated in solution. The lanthanoids can coordinate three oxydiacetate² and dipicolinate¹ ligands, indicating a coordination number of at least nine in solution. The maximum number of oxalate groups coordinated is four⁶, a fact which also implies a coordination number larger than six. Also scandium(III) coordinates four oxalate ions, whereas only three malonate ions are bound.⁷ It is thus of interest to determine the maximum number of coordinated malonate ions for the rare earth elements to see whether the difference between the number of coordinated oxalate and malonate ions is due to the ligand or to the size of the central ion.

Discussion along the lines mentioned should be facilitated if more than one characteristic of the reactions is studied. We have for this reason studied both the free energy and enthalpy changes for most of the systems.

This paper will describe the stoichiometric composition and the stability constants for the complexes formed between the various lanthanoids and the ligands malonate and hydrogen malonate. There are some earlier communications on this subject. Ke *et al.*⁹ have studied rare earth bimalonate complexes using an ion-exchange method and reported stability constants for the complexes MHA and M(HA)₂. Powell *et al.*¹⁰ have used the same potentiometric method as the present authors and found evidence for the formation of the species MA and MA₂. Only Paramonova *et al.*¹¹ have clearly taken into consideration the fact that both malonate and bimalonate ions act as ligands to lanthanoid ions.

None of the studies published so far have shown the existence of complexes with more than two malonate ions coordinated.

The method chosen for the present study was one of the potentiometric standard methods, *viz.* the determination of the concentration of free hydrogen ion by means of a glass electrode.

All measurements refer to a sodium perchlorate medium with a constant sodium ion concentration equal to 1.00 M and a temperature of 25.0°C.

NOTATIONS

Malonic acid, CH₂(COOH)₂, is written as H₂A. C_M, C_H, C_A denote the total concentration of metal ion, free and dissociable hydrogen ions, and malonate ion, respectively. *m*, *h*, *a*, denote the concentrations of free metal ion, hydrogen ion, and malonate ion, respectively.

$\beta_{p,q,r}$ = the over-all stability constant for the complex M_pH_qA_r, defined as

$$\beta_{p,q,r} = [\text{M}_p\text{H}_q\text{A}_r] m^{-p} h^{-q} a^{-r}; p \geq 0, q \geq 0, r \geq 0, p + q + r \geq 2$$

$$\bar{n} = (C_A - \sum_{j=0}^2 [\text{H}_j\text{A}]) / C_M$$

$\bar{n}_H$ = the mean number of hydrogen ions bound per malonate ion, *i.e.*

$$\bar{n}_H = (C_H - h)/C_A$$

$\alpha_{p,q,r}$ = the fraction of the total metal ion concentration existing as the complex $M_pH_qA_r$,

$$\alpha_{p,q,r} = p[M_pH_qA_r]/C_M$$

V_0 = the initial volume of the titrand solution.

v = the added volume of the titrator solution.

CALCULATION OF THE STABILITY CONSTANTS

The complex formation in the lanthanoid malonate systems has been studied by measuring the change in hydrogen ion concentration when a solution of the metal ion is titrated with a buffer of the ligand and its corresponding acid. This is a standard method, often used in systems where the ligand is the anion of a weak acid and where suitable electrodes, reversible with respect to the metal ion, are lacking.

From the total concentrations C_M , C_H , and C_A and the concentration of free hydrogen ion, h , one can compute the quantities a^* and $\bar{n}^*$ given below:

$$a^* = (C_H - h)/(\beta_{0,1,1}h + 2\beta_{0,2,1}h^2) \quad (1)$$

$$\bar{n}^* = [C_A - a^* (1 + \beta_{0,1,1}h + \beta_{0,2,1}h^2)]/C_M \quad (2)$$

If all complexes formed are of the type MA_r , $r = 1, \dots, N$, the left members of eqns. (1) and (2) are equal to a and $\bar{n}$, respectively. The stability constants can be calculated from corresponding values of $\bar{n}$ and a . The possible existence of acid or polynuclear complexes of the type $M_pH_qA_r$ is often checked by determining the function $\bar{n}^*$ (a^*) in solutions where the total concentrations C_M , C_H , and C_A are varied systematically. If $\bar{n}^*$ (a^*) turns out to depend on C_H and/or C_M this is taken as an indication of the existence of species other than MA_r .

A graphical integration method due to Österberg² can in some cases be used to calculate the concentration of free ligand. Values of a/a_0 , where a_0 is an integration constant, are obtained. In order to determine a_0 , the measurements must be extended to a high hydrogen ion concentration, h_0 , where all metal complex formation is completely suppressed. This gives $a_0 = C_A/(1 + \beta_{0,1,1}h_0 + \beta_{0,2,1}h_0^2)$. In the present case, however, it was not experimentally possible to measure h accurately in such strongly acidic solutions.

The various stability constants were instead obtained by using a computer and a least-squares program in the series "Letagrop Vrid", written by Ingri and Sillén.¹³ As starting values of $\beta_{p,q,r}$ we used estimates of $\beta_{1,0,r}$ obtained from $\bar{n}^* - a^*$ data in solutions with low hydrogen ion concentrations. Starting values of the constants $\beta_{1,1,1}$ were obtained by assuming that the complexes formed between the lanthanoids and hydrogen malonate ion had the same strength as the corresponding acetate complexes.^{14,15} C_H/C_A was chosen as the error-carrying variable. The "best" set of constants was the one that minimized the error square sum U , given by

$$U = \sum_i [(C_{H,i,\text{calc}} - C_{H,i,\text{exp}})/C_{A,i}]^2$$

where $C_{H,i,calc}$ is the value of the total hydrogen ion concentration calculated from $C_{A,i}$, $C_{M,i}$, h , and the values of $\beta_{p,q,r}$. The summation is taken over all experimental points "i", all of which were given the weight one.

Some properties of $\bar{n}^=f(a^*)$ curves.* It may in some cases be difficult to interpret titration data obtained by using the method described here. It is, for instance, easy to overlook the existence of mixed complexes, and this seems to have been done in some investigations of the complex formation between the rare earths and the dicarboxylates which we are presently studying.¹⁶ The following discussion will point out some of the reasons for these misinterpretations.

If it is assumed that a system forms complexes only of the type MA_r , a and $\bar{n}$ can be calculated from eqns. (1) and (2) and $\bar{n}$ is a function of a only. The experimental proof of the assumption is often given by showing that the curves $\bar{n}=f(a)$ coincide in solutions with different compositions. However, if an acid complex is formed, the experimentally determined quantities are $\bar{n}^*$ and a^* . Therefore, one must know the properties of the function $\bar{n}^*(a^*)$ under different experimental conditions. This will be discussed in the following example.

For simplicity we assume that only two metal complexes, MA and MHA , are formed in a system. The ligand A forms two complexes with protons, viz. HA and H_2A . Eqns. (3) and (4) give the relations between a and a^* , and $\bar{n}$ and $\bar{n}^*$, respectively.

$$a/a^* = 1 - \beta_{1,1,1} m / (\beta_{0,1,1} + 2\beta_{0,2,1} h + \beta_{1,1,1} m) \quad (3)$$

$$\bar{n}^* = \bar{n} + \frac{\beta_{1,1,1} m a (\beta_{0,2,1} h^2 - 1)}{C_M (\beta_{0,1,1} + 2\beta_{0,2,1} h)} + \frac{[MHA]}{C_M} \quad (4)$$

In solutions where C_H is small enough compared to C_A , the term $2\beta_{0,2,1} h$ will be negligible in comparison with $\beta_{0,1,1}$, and $\beta_{0,2,1} h^2$ much smaller than unity. Eqns. (3) and (4) can then be written as $a^*/a = 1 + \beta_{1,1,1} m \beta_{0,1,1}^{-1}$ and $\bar{n}^* = \bar{n}(1 - \beta_{1,1,1} \beta_{0,1,1}^{-1} \beta_{1,0,1}^{-1})$, respectively. For a given value of a^* , the value of $1 + \beta_{1,1,1} m \beta_{0,1,1}^{-1}$ does not vary very much in solutions where the previous approximations are valid. This means that it is possible to get an $\bar{n}^*$ vs. a^* curve, independent of the ratio C_H/C_A , as long as the ratio is small. In the lutetium system (*vide infra* p. 1394) this occurs when the ratio C_H/C_A is smaller than 1:2 (*cf.* Fig. 2).

The above discussions can be formulated quantitatively by studying the variation of the constant β^* , obtained from the $\bar{n}^*$ vs. a^* data. β^* is defined as

$$\beta^* = (\bar{n}^* \times C_M) / (m^* \times a^*)$$

and can be expressed as

$$\beta^* = \left[\frac{(\beta_{0,1,1} + 2h\beta_{0,2,1})\beta_{1,0,1} + \beta_{1,1,1}(\beta_{0,2,1}h^2 - 1)}{\beta_{0,1,1} + 2h\beta_{0,2,1} + m\beta_{1,1,1}} \right] \frac{m}{m^*} \quad (5)$$

It is difficult to estimate how the value of β^* varies during a titration by studying eqn. (5). We have therefore calculated the variation of β^* for two different hypothetical complex systems with the composition of the buffer

used. The value of C_M has been constant, equal to 20 mM, and the ratio C_H/C_A has been varied between 3:2 and 1:10.

System 1 has the following constants: $\beta_{1,0,1} = 7.6 \times 10^3 \text{ M}^{-1}$, $\beta_{1,1,1} = 1.8 \times 10^6 \text{ M}^{-2}$, $\beta_{0,1,1} = 1.0 \times 10^5 \text{ M}^{-1}$, $\beta_{0,2,1} = 4.5 \times 10^7 \text{ M}^{-2}$.

System 2 has the same values of $\beta_{1,0,1}$ and $\beta_{1,1,1}$, while the values of $\beta_{0,1,1}$ and $\beta_{0,2,1}$ are $4.0 \times 10^5 \text{ M}^{-1}$ and $1.5 \times 10^7 \text{ M}^{-2}$, respectively. The calculated values of β^* as a function of $\bar{n}^*$ are given in Fig. 1 for the various values of C_H/C_A used.

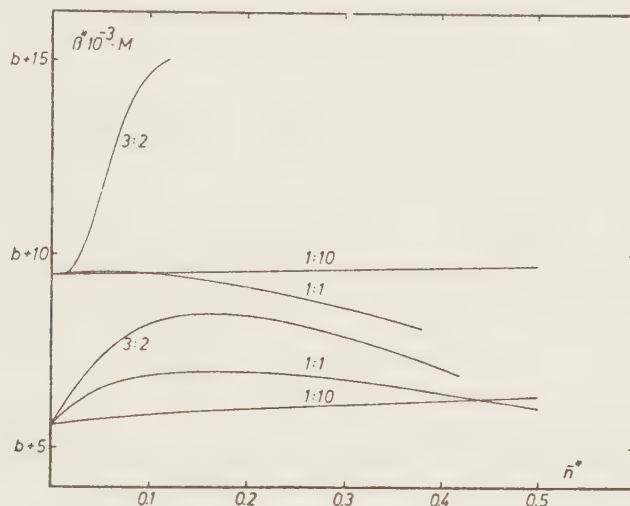


Fig. 1. β^* as a function of $\bar{n}^*$ for system 1 (lower curves) and system 2 (upper curves).

The constants of the systems are given above.

The ratio C_H/C_A is indicated at each curve. b equals zero for system 1 and -2.5 for system 2. The curves are drawn to $\bar{n}^* = 0.5$ or $C_A = 100 \text{ mM}$.

In the region $0.1 < \bar{n}^* < 0.5$, the total variation of β^* is 10 % for the 1:10 buffer in system 1, and 4 % in system 2. The experimental data can thus be described by assuming only one complex MA with, for system 1, a stability constant equal to $(6.0 \pm 0.3) \times 10^3 \text{ M}^{-1}$. When an actual titration is performed, the ratio C_H/C_A is usually not constant, due to the presence of an excess of acid in the metal stock solutions. This fact can make the apparent constancy of β^* even better. If an S-solution with $C_M = 20 \text{ mM}$ and $C_H = 0.2 \text{ mM}$ is titrated with a buffer solution where C_H/C_A is equal to 1:3, the measurements can be described by a constant β^* equal to $(6.2 \pm 0.2) \times 10^3 \text{ M}^{-1}$ in the region $0.05 < \bar{n}^* < 0.9$. If the concentration of acid in the metal solution is high, and the ratio C_H/C_A in the buffer is small, the calculated values of β^* will decrease monotonously when $\bar{n}^*$ increases.

When the values of C_A are small, eqn. (5) is reduced to

$$\beta^* \approx \frac{(\beta_{0,1,1} + 2h\beta_{0,2,1})\beta_{1,0,1} + \beta_{1,1,1}(\beta_{0,2,1}h^2 - 1)}{\beta_{0,1,1} + 2h\beta_{0,2,1} + C_M\beta_{1,1,1}} \quad (6)$$

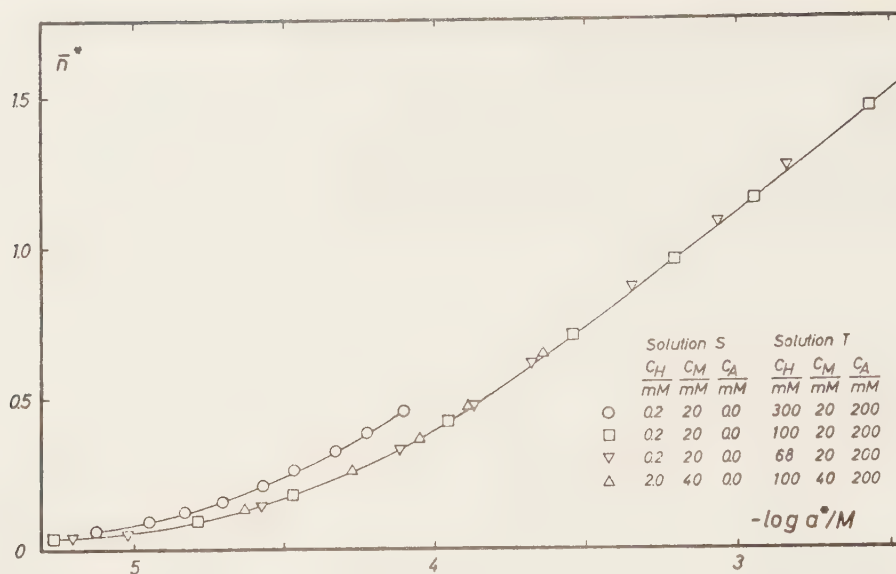


Fig. 2. Experimental $\bar{n}^*$ vs. $-\log(a^*/M)$ curves for the lutetium malonate system.

It is in principle possible to calculate the constants $\beta_{1,1,1}$ and $\beta_{1,0,1}$ from this relation by measurements of β^* at various values of h and C_M . In actual practice, one finds that it is not possible to determine small values of $\bar{n}^*$ with a sufficiently high accuracy to permit the use of eqn. (6).

The following conclusion can be drawn from this discussion.

a. When complex formation is studied, using hydrogen ion as a competitor, in a system where the ligand A is a polyprotic base, the possibility that the species H_nA act as ligands must be kept in mind.

b. It is possible to get an $\bar{n}^*$ vs. a^* curve independent of C_H even in the presence of mixed complexes of the type MH_nA_r . The fact that the curve can be described with a set of stability constants $\beta_{1,0,r}$ is no conclusive proof of the non-existence of mixed complexes.

c. The variations in the total hydrogen ion concentration in the solutions used must be made as large as the experimental technique allows.

d. At low values of $\bar{n}^*$ it is easier to see variations in the function $\bar{n}^*/a^*$ vs. a^* than in $\bar{n}^*$ vs. a^* .

EXPERIMENTAL

Chemicals used. Sodium perchlorate was prepared from perchloric acid (Baker's Analyzed) and sodium carbonate (Merck p.a.), as described by Gerding.¹⁷

Lanthanum perchlorate was prepared from the carbonate (Fluka p.a.). Cerium(III) perchlorate was prepared in the following way: a solution of cerium(IV) sulfate (Merck p.a.) was reduced with hydrogen peroxide. The sulfate ions were then precipitated by adding barium perchlorate, and the cerium(III) hydroxide was precipitated by ammonia. The precipitate was dissolved in perchloric acid, and then the cerium was precipitated with ammonium carbonate. An 0.2 M cerium perchlorate stock solution was prepared

by dissolving the carbonate in perchloric acid. Stock solutions of the other rare earth perchlorates were made by dissolving the oxide (Lindsay Chemical Co., > 99.9 %) in warm perchloric acid. The metal content of the solutions was determined by titration with EDTA in urotropin buffer, using xylenolorange as indicator (*cf.* Ref. 18). The hydrogen ion concentration of the solutions was approximately 0.02 M, the exact values being determined potentiometrically.

Malonic acid (Fischer Sci. Co.) was purified by repeated recrystallization from diethyl ether. The formula weight as determined by alkalimetric titration was 104.3 (calc. 104.1).

The various malonate buffer solutions were prepared by mixing appropriate amounts of stock solutions of malonic acid and disodium malonate. The latter solution was prepared by neutralizing malonic acid to 99 % with sodium hydroxide. The small excess of acid was determined potentiometrically.

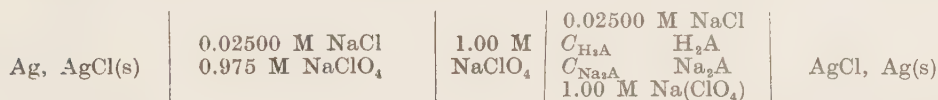
Potentiometric measurements. The emf E of galvanic cells of the following type was measured:



The solution in the right half-cell was prepared by adding known amounts of a solution T from a piston burette to a known volume of a solution S. The additions were made with an error of at most 0.005 ml. The value of C_M was constant during a titration series. The system was calibrated before each titration by measuring the emf, E_R , when the right half-cell of (7) contained a solution with known hydrogen ion concentration, h_R . The unknown hydrogen ion concentration, h , is then calculated from eqn. (8),

$$-59.16 \log h/h_R = (E_R/mV - E_j'/mV) - (E/mV - E_j''/mV) \quad (8)$$

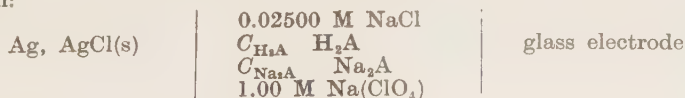
where E_j' and E_j'' are liquid junction potentials. The liquid junction potentials depend both on the hydrogen ion concentration and on the perchlorate ion (or the malonate ion) concentration in the solution, *i.e.* $E_j = E_{h,j} + E_{a,j}$. The hydrogen ion concentration dependent term, $E_{h,j}$, was determined as described by Ahrlund and Rosengren.¹⁹ The perchlorate ion concentration dependent term, $E_{a,j}$, was determined from emf measurements of cells of the following type:



The term $E_{a,j}$ is only of importance when a fairly large part of the sodium perchlorate has been exchanged with sodium malonate and is equal to 0.8 mV when C_{NaClO_4} is 0.900 M.

The liquid junction potentials were measured by using a Jena glass electrode of the "Thalamide" type and a Fluke 885 AB differential voltmeter. A Beckman glass electrode (type 40498) and a Radiometer pHM4d pH-meter were used in the other titrations. The Ag,AgCl electrodes were prepared according to Brown.²⁰ A quinhydrone electrode did not work well in these solutions. The reproducibility of the emf was usually within 0.1 mV. The temperature was controlled within $\pm 0.1^\circ\text{C}$ by using a water thermostat.

The proton malonate system was examined in a cell of type (7) with $C_M = 0$, and using different constant values of C_A , *viz.* 10, 50, and 100 mM, respectively. After correction for the liquid junction potential, all titration series could be described with the same set of proton-malonate stability constants. If $E_{a,j}$ is neglected, the stability constants increase about 5 % as C_A increases from 10 mM to 100 mM. This result was confirmed by measurements in a cell without liquid junction potential. This cell had the following composition:



The lanthanoid-malonate systems were measured in galvanic cells of the type (7), where the total concentrations C_M , C_H , and C_A were known, and h was determined.

The formation of a slightly soluble compound of the composition $M_2A_3 \cdot nH_2O$ complicated the measurements. The solubility is smallest for the light lanthanoids. No quantitative determination of the solubility has been made, but the heaviest elements can be titrated in solutions with $C_M = 15$ mM, whereas lanthanum and cerium form a precipitate in solutions with $C_M < 2.5$ mM.

The minimum solubility occurs when $\bar{n}$ equals 1.5. When a metal solution is titrated with a malonate buffer, the precipitate is formed before $\bar{n}$ reaches this value, and $\beta_{1,0,3}$ can thus not be determined from these data. In order to obtain information on $\beta_{1,0,3}$ some titrations have been made by adding an acid buffer to a metal solution with a high ligand concentration. In this way some $\bar{n}$ -values in the region $1.8 < \bar{n} < 2.5$ were obtained. These solutions are supersaturated, and a precipitate is easily formed. The precision in these determinations is also lower than in the region of low $\bar{n}$ -values.

RESULTS

The proton-malonate system. All data could be described by assuming the existence of two acidic species, HA and H_2A . The stability constants have been calculated *via* graphical integration of the curve $\bar{n}_H/h$ *vs.* h and by the least-squares program "Letagrop Vrid". The stability constants as calculated by the graphical method were:

$$\beta_{0,1,1} = (1.155 \pm 0.010) \times 10^5 \text{ M}^{-1}$$

$$\beta_{0,2,1} = (4.49 \pm 0.08) \times 10^7 \text{ M}^{-2}$$

The quoted errors are estimated maximum errors. This set of constants has been used for the later calculations.

The least-squares method gave the following values:

$$\beta_{0,1,1} = (1.158 \pm 0.005) \times 10^5 \text{ M}^{-1}$$

$$\beta_{0,2,1} = (4.51 \pm 0.03) \times 10^7 \text{ M}^{-2}$$

The quoted errors here and in the following are equal to three standard deviations. The standard deviation in C_H/C_A was 2.91×10^{-3} . The calculation was based on 13 different titration series with a total of 288 experimental values.

The proton-malonate complexes have been studied by Szilard²¹ at 20°C in 1 M NaClO₄. A recalculation of his measurements to 25°C by using the known enthalpy values for the protonation reactions⁷ gave values which agreed within 1 % with our constants.

We have assumed that the constants remain the same when $C_M \neq 0$ as when $C_M = 0$.

The lanthanoid-malonate systems. Fig. 2 shows some experimental values of $\bar{n}^*$ *vs.* $-\log(a^*/M)$ for the lutetium malonate system. The values of a^* and $\bar{n}^*$ have been calculated from eqns. (1) and (2). The experimental material was obtained from three titration series with C_M equal to 20 mM, and the ratio C_H/C_A in the T-solution equal to 3:2, 1:2, and 1:3, respectively. A fourth series had C_M equal to 40 mM, and C_H/C_A equal to 1:2. For the series with $C_H/C_A > 1/2$ (but not for those with $C_H/C_A \leq 1/2$), the experiments show clearly that $\bar{n}^*$ is a function of both a^* and h , *i.e.* complexes containing both A and

Table 1. Experimental results for the lanthanum and lutetium malonate systems. The results are given as v/ml , $(E-E_i)/\text{mV}$, $\bar{n}_\text{H}$, $(\bar{n}_\text{H,calc}-\bar{n}_\text{H,exp}) \times 10^3$. The sodium ion concentration is 1.00 M in all solutions. Approximately one half of the experimental results is given.

a. The lanthanum malonate system

Series 1. S: $C_\text{H}=0.06132$ M, $C_\text{M}=0.01372$ M, $C_\text{A}=0.03020$ M, $C_{\text{NaClO}_4}=1.000$ M;
T: $C_\text{H}=0.00128$ M, $C_\text{M}=0.01371$ M, $C_\text{A}=0.03027$ M, $C_{\text{NaClO}_4}=0.940$ M;
 $V_0=19.97$ ml, $E_0=500.0$ mV;

0.000,	379.1,	1.731,	6.09;	3.000,	363.8,	1.605,	-2.90;
6.000,	351.0,	1.470,	-1.29;	9.000,	340.0,	1.347,	0.78;
12.00,	330.1,	1.239,	0.28;	15.00,	321.2,	1.145,	0.68;
18.00,	313.2,	1.064,	2.82;	21.00,	305.9,	0.993,	5.39;
24.00,	299.0,	0.931,	6.02;				

Series 2. S: $C_\text{H}=0.1217$ M, $C_\text{M}=0.01372$ M, $C_\text{A}=0.06040$ M, $C_{\text{NaClO}_4}=1.000$ M;
T: $C_\text{H}=0.00164$ M, $C_\text{M}=0.01371$ M, $C_\text{A}=0.06038$ M, $C_{\text{NaClO}_4}=0.879$ M;
 $V_0=19.97$ ml, $E_0=500.4$ mV;

0.000,	389.1,	1.797,	8.56;	1.500,	378.7,	1.731,	3.48;
4.500,	361.0,	1.577,	0.23;	7.500,	347.1,	1.430,	0.69;
10.50,	335.4,	1.303,	0.66;	13.50,	325.1,	1.195,	1.84;

Series 3. S: $C_\text{H}=0.000510$ M, $C_\text{M}=0.009138$ M, $C_\text{A}=0.000$ M, $C_{\text{NaClO}_4}=1.000$ M;
T: $C_\text{H}=0.02156$ M, $C_\text{M}=0.009138$ M, $C_\text{A}=0.1625$ M, $C_{\text{NaClO}_4}=0.680$ M;
 $V_0=20.01$ ml, $E_0=385.8$ mV;

0.200,	133.5,	0.413,	-0.52;	0.300,	123.1,	0.327,	-1.40;
0.400,	116.5,	0.281,	-0.56;	0.500,	111.5,	0.252,	-0.91;
0.600,	107.5,	0.233,	-1.11;	0.700,	104.2,	0.219,	-0.75;

Series 4. S: $C_\text{H}=0.000510$ M, $C_\text{M}=0.009138$ M, $C_\text{A}=0.000$ M, $C_{\text{NaClO}_4}=1.000$ M;
T: $C_\text{H}=0.02134$ M, $C_\text{M}=0.009138$ M, $C_\text{A}=0.1415$ M, $C_{\text{NaClO}_4}=0.720$ M;
 $V_0=20.02$ ml, $E_0=385.8$ mV;

0.100,	158.5,	0.668,	-0.27;	0.200,	138.8,	0.464,	-0.65;
0.300,	128.4,	0.370,	-0.85;	0.400,	121.7,	0.319,	-1.14;
0.500,	116.9,	0.287,	-0.63;	0.600,	113.1,	0.265,	-0.39;
0.700,	110.1,	0.249,	0.97;	0.800,	107.2,	0.237,	-0.05;
0.900,	104.9,	0.228,	0.96,	1.000,	102.7,	0.221,	1.11;

b. The lutetium malonate system

Series 1. S: $C_\text{H}=0.000200$ M, $C_\text{M}=0.01990$ M, $C_\text{A}=0.000$ M, $C_{\text{NaClO}_4}=1.000$ M;
T: $C_\text{H}=0.1018$ M, $C_\text{M}=0.01990$ M, $C_\text{A}=0.2014$ M, $C_{\text{NaClO}_4}=0.699$ M;
 $V_0=20.11$ ml, $E_0=472.4$ mV;

0.200,	274.0,	0.382,	3.19;	0.400,	276.3,	0.432,	-3.50;
0.800,	276.3,	0.468,	-9.50;	1.300,	274.5,	0.484,	-11.29;
2.000,	271.0,	0.494,	-10.49;	2.500,	268.3,	0.498,	-7.37;
3.000,	265.3,	0.500,	-5.44;	3.500,	262.2,	0.502,	-3.46;
4.000,	259.0,	0.503,	-2.17;	4.500,	255.9,	0.504,	-0.54;
5.000,	252.8,	0.505,	0.15;	6.000,	247.4,	0.505,	3.49;

Series 2. S: $C_\text{H}=0.00020$ M, $C_\text{M}=0.01991$ M, $C_\text{A}=0.000$ M, $C_{\text{NaClO}_4}=1.000$ M;
T: $C_\text{H}=0.06833$ M, $C_\text{M}=0.01981$ M, $C_\text{A}=0.2007$ M, $C_{\text{NaClO}_4}=0.667$ M;
 $V_0=20.11$ ml, $E_0=474.9$ mV;

0.300,	267.7,	0.301,	-5.13;	0.750,	266.7,	0.325,	-8.39;
1.000,	265.4,	0.330,	-7.72;	1.500,	262.0,	0.336,	-6.83;
2.000,	258.1,	0.339,	-4.23;	3.010,	249.1,	0.341,	2.17;
4.000,	239.5,	0.342,	4.55;	5.000,	230.6,	0.343,	4.38;

Table 1. Continued.

Series 3. S: $C_H = 0.00171$ M, $C_M = 0.03964$ M, $C_A = 0.000$ M, $C_{NaClO_4} = 1.000$ M;
 T: $C_H = 0.1031$ M, $C_M = 0.03961$ M, $C_A = 0.2011$ M, $C_{NaClO_4} = 0.702$ M;
 $V_0 = 20.11$ ml, $E_0 = 475.0$ mV;

1.000,	299.7,	0.569,	20.91;	2.000,	295.7,	0.547,	13.17;
3.000,	292.7,	0.538,	10.89;	4.000,	290.1,	0.533,	11.68;
6.000,	285.3,	0.523,	14.96;				

Series 4. S: $C_H = 0.05165$ M, $C_M = 0.01943$ M, $C_A = 0.02525$ M, $C_{NaClO_4} = 1.000$ M;
 T: $C_H = 0.00141$ M, $C_M = 0.01943$ M, $C_A = 0.02515$ M, $C_{NaClO_4} = 0.950$ M;
 $V_0 = 20.11$ ml, $E_0 = 386.1$ mV;

0.000.	265.7,	1.680,	13.39;	1.500,	259.8,	1.618,	12.73;
3.000.	254.1,	1.556,	4.98;	4.500,	249.1,	1.491,	1.22;
6.000,	244.8,	1.428,	2.06;	7.500,	240.8,	1.368,	0.17;
9.000,	237.2,	1.312,	-0.94;	10.50,	234.0,	1.258,	-0.13;
12.00,	230.9,	1.210,	-2.63;	13.50,	228.1,	1.164,	-3.49;
15.00,	225.6,	1.121,	-2.17;	16.50,	223.1,	1.081,	-4.06;
18.00,	220.9,	1.044,	-2.93;	19.50,	218.8,	1.009,	-2.32;
21.00,	216.7,	0.977,	-3.75;				

Series 5. S: $C_H = 0.00020$ M, $C_M = 0.01990$ M, $C_A = 0.000$ M, $C_{NaClO_4} = 1.000$ M;
 T: $C_H = 0.3024$ M, $C_M = 0.01990$ M, $C_A = 0.2010$ M, $C_{NaClO_4} = 0.900$ M;
 $V_0 = 20.11$ ml, $E_0 = 472.7$ mV;

0.500,	315.4,	1.095,	13.42;	1.000,	321.5,	1.233,	3.39;
1.600,	324.8,	1.304,	1.26;	3.000,	328.1,	1.373,	2.76;
4.000,	329.1,	1.397,	2.91;	6.000,	330.1,	1.424,	4.46;
9.000,	330.6,	1.443,	5.65;	13.00,	330.9,	1.455,	9.17;
18.00,	330.9,	1.463,	10.64;	25.00,	330.8,	1.469,	11.93;

Series 6. S: $C_H = 0.02592$ M, $C_M = 0.01943$ M, $C_A = 0.02520$ M, $C_{NaClO_4} = 0.974$ M;
 T: $C_H = 0.00141$ M, $C_M = 0.01943$ M, $C_A = 0.02515$ M, $C_{NaClO_4} = 0.950$ M;
 $V_0 = 21.00$ ml, $E_0 = 386.6$ mV;

3.000,	209.8,	0.866,	-7.10;	6.000,	203.6,	0.781,	-9.72;
9.000,	198.3,	0.711,	-9.95;	12.00,	193.6,	0.654,	-9.91;
18.00,	185.6,	0.564,	-9.03;	24.00,	178.9,	0.498,	-8.64;
30.00,	173.2,	0.447,	-8.33;	36.00,	168.3,	0.407,	-7.91;

Series 7. S: $C_H = 0.1027$ M, $C_M = 0.01943$ M, $C_A = 0.05078$ M, $C_{NaClO_4} = 1.000$ M;
 T: $C_H = 0.00167$ M, $C_M = 0.01934$ M, $C_A = 0.05038$ M, $C_{NaClO_4} = 0.900$ M;
 $V_0 = 20.01$ ml, $E_0 = 386.4$ mV;

1.500,	266.6,	1.699,	7.40;	3.000,	259.0,	1.626,	1.69;
4.500,	252.4,	1.552,	-2.47;	6.000,	246.9,	1.480,	-1.44;
7.500,	241.9,	1.412,	-2.68;	9.000,	237.5,	1.349,	-2.26;
10.50,	233.5,	1.290,	-1.78;	12.00,	229.9,	1.236,	0.05;
13.50,	226.3,	1.186,	-2.23;	15.00,	223.1,	1.140,	-1.42;
18.00,	217.0,	1.057,	-2.60;	21.00,	211.4,	0.986,	-3.39;

H must be formed. The curves obtained at C_M equal to 20 mM and 40 mM are very nearly the same, indicating the absence of polynuclear species. The highest value for $\bar{n}^*$ is 2.7 in this system, that is, complexes with at least three malonate ions per metal ion must be formed. A first attempt to interpret the experimental data was made by assuming the formation of the complexes MHA, MA, MA_2 , and MA_3 . The calculations were made by using the least-squares program.

The first least-squares refinement showed the presence of a systematic error, the differences $(C_H/C_A)_{\text{calc}} - (C_H/C_A)_{\text{exp}}$, increasing with increasing concentration of free ligand. This systematic difference became much smaller when a complex MHA_2 was included in the refinements.

Other types of complexes are also possible. The terbium system was investigated to see if inclusion of the binuclear complex M_2A gave a better description of the data. The stability constant $\beta_{2,0,1}$ obtained was $(2.6 \pm 10.0) \times 10^3 \text{ M}^{-2}$. A similar test for the complex MH_2A_2 was performed for the dysprosium and lutetium systems. The calculated constants $\beta_{1,2,2}$ became $(4.0 \pm 2.0) \times 10^{12} \text{ M}^{-4}$ for dysprosium and $(2.5 \pm 2.7) \times 10^{12} \text{ M}^{-4}$ for lutetium. The standard deviations in C_H/C_A decreased from 4.75×10^{-3} to 3.86×10^{-3} , and from 8.73×10^{-3} to 8.19×10^{-3} , respectively. All other constants had practically the same values as in the calculation, where $\beta_{1,2,2}$ was not included. However, their standard deviations had increased with as much as 50 %. It can thus be concluded that inclusion of the constants $\beta_{2,0,1}$ and $\beta_{1,2,2}$ does not improve the description of the experimental data to a significant extent. The complexes M_2A and MH_2A_2 do not occur in any significant amounts, if at all, in the solutions studied.

All experimental results have thus been described by using only the complexes MA, MA_2 , MA_3 , MHA, and MHA_2 . The corresponding stability constants with their estimated errors, equal to three standard deviations, are given in Table 2. The experimental difficulties mentioned before (see p. 1394) made a

Table 2. Stability constants for the lanthanoid malonate systems. The errors are equal to three standard deviations.

Metal ion	Number of experimental points	Standard deviation in C_H/C_A	$\beta_{1,0,1} \times 10^{-2} \text{ M}$	$\beta_{1,0,2} \times 10^{-6} \text{ M}^2$	$\beta_{1,0,3} \times 10^{-7} \text{ M}^3$	$\beta_{1,1,1} \times 10^{-6} \text{ M}^2$	$\beta_{1,1,2} \times 10^{-9} \text{ M}^3$
La	56	4.51×10^{-3}	1.167 ± 0.034	0.139 ± 0.043		2.03 ± 0.26	1.51 ± 0.36
Ce	50	5.42×10^{-3}	1.79 ± 0.07	0.17 ± 0.09		2.41 ± 0.34	2.0 ± 0.7
Pr	98	10.3×10^{-3}	1.96 ± 0.17	0.41 ± 0.36		2.97 ± 0.28	1.8 ± 1.1
Nd	43	1.83×10^{-3}	2.390 ± 0.041	0.830 ± 0.041		3.01 ± 0.17	2.76 ± 0.34
Sm	119	9.91×10^{-3}	4.73 ± 0.16	1.18 ± 0.29		3.94 ± 0.37	7.2 ± 2.1
Eu	82	5.65×10^{-3}	5.25 ± 0.17	1.74 ± 0.21		3.0 ± 0.5	9.7 ± 1.6
Gd	160	10.8×10^{-3}	5.39 ± 0.18	1.74 ± 0.35		3.17 ± 0.28	6.0 ± 1.3
Tb	88	4.94×10^{-3}	6.55 ± 0.16	2.39 ± 0.23		2.33 ± 0.37	12.3 ± 1.7
Dy	74	4.75×10^{-3}	7.05 ± 0.15	2.23 ± 0.20	3.9 ± 1.6	2.03 ± 0.24	6.5 ± 1.8
Ho	83	4.12×10^{-3}	6.79 ± 0.16	2.34 ± 0.16	4.7 ± 1.2	2.02 ± 0.29	9.0 ± 1.3
Er	134	3.77×10^{-3}	7.09 ± 0.13	2.43 ± 0.15	4.1 ± 0.7	2.23 ± 0.24	8.5 ± 1.0
Tm	116	3.73×10^{-3}	7.01 ± 0.14	2.64 ± 0.14	4.2 ± 0.8	1.84 ± 0.25	9.6 ± 1.1
Yb	94	3.45×10^{-3}	7.42 ± 0.15	2.71 ± 0.13	6.0 ± 1.0	1.63 ± 0.22	5.8 ± 1.0
Lu	150	8.73×10^{-3}	7.57 ± 0.22	2.60 ± 0.25	7.6 ± 1.6	1.77 ± 0.25	3.2 ± 1.9

determination of $\beta_{1,0,3}$ impossible for the elements lanthanum to terbium. Tables 1a and 1b give the experimental results for the titrations with lanthanum and lutetium. Fig. 3 shows the relative amounts of the various complexes at different values of h and a .

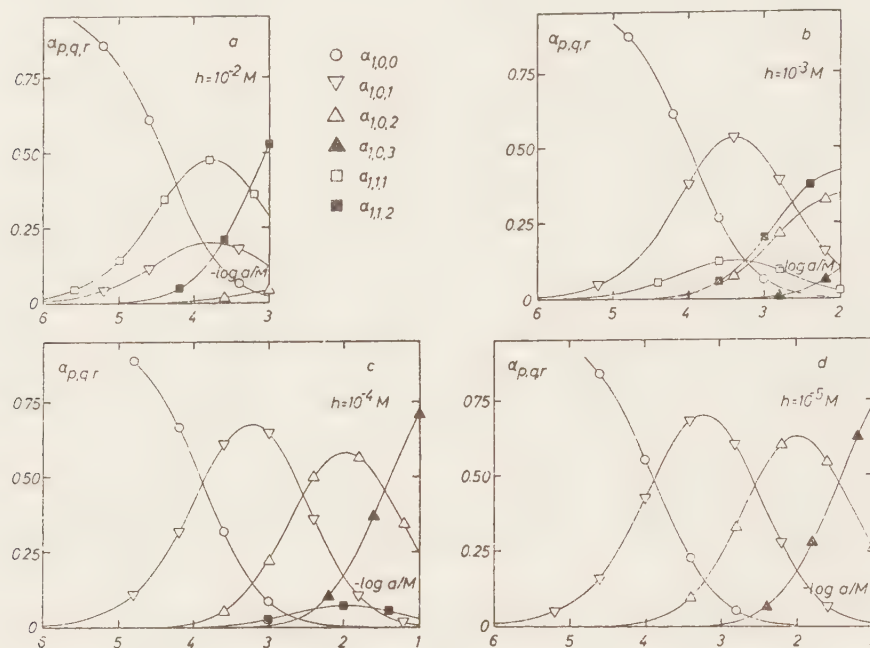


Fig. 3. The relative amounts of the different complexes in the lutetium malonate system at four different values of the hydrogen ion concentration.

DISCUSSION

Even with due allowance for the differences in experimental conditions, the results of Ke *et al.*⁹ for acid complexes are not in agreement with those given here.

Powell *et al.*¹⁰ have determined $\beta_{1,0,1}$ and $\beta_{1,0,2}$ for lanthanoid-malonate complexes in 0.1 M KNO₃ at 25°C with the same potentiometric method as used here. Powell does not report any acid complexes, but because of lack of primary data it is not possible to make any close comparison.

Paramonova *et al.*¹¹ give the following constants for the europium system:

$$\beta_{1,0,1} = (4.0 \pm 0.2) \times 10^3 \text{ M}^{-1}, (\beta_{1,1,1}/\beta_{0,1,1}) = 17.5 \pm 2.0 \text{ M}^{-1}$$

The determination refers to 0.5 M NaNO₃ and an ion-exchange method was used. The temperature is not given. The corresponding values found here are:

$$\beta_{1,0,1} = (5.25 \pm 0.17) \times 10^3 \text{ M}^{-1}, (\beta_{1,1,1}/\beta_{0,1,1}) = 26 \pm 4 \text{ M}^{-1}$$

A more detailed discussion will be postponed until the experimental results from the enthalpy measurements have been presented. Some comparisons with a few other carboxylate complexes will, however, be made.

The complex formation in some lanthanoid-oxalate complexes have been studied by Grenthe *et al.*⁶ The oxalate complexes are stronger than the corresponding malonate complexes *i.e.* the five-membered chelate ring in the former complexes is more stable than the six-membered one in the latter complexes. There is no tendency for the formation of acid complexes in the oxalate systems. However, such complexes are formed with the weaker chelated malonate ligand.

A maximum of four oxalate groups are coordinated to the lanthanoid ions, but in the malonate systems there are no indications for the formation of a fourth complex. In the oxydiacetate systems the ratio between the second and third stepwise stability constants, K_2/K_3 , increases considerably with decreasing ionic radius, indicating an increasing difficulty for the last complex to be formed. Neither the oxalate nor the malonate systems show any "steric effect" of this kind.

Acetate ion and bimalonate ion act in a similar way as ligands to lanthanoids. The acetate complexes are somewhat stronger, which might be correlated with the higher basicity of the acetate ion compared to the bimalonate ion.

The strength of the acid MHA increases from lanthanum to lutetium. This might be regarded as an effect of the change in electrostatic interaction between proton and metal ion, when the radius of the metal ion diminishes. pK_a for this acid lies in the range from 3.2 to 2.3. It is a much stronger acid than the hydrogen malonate ion. The acidity is comparable to that of malonic acid itself, for which pK_a is 2.46. This suggests that the tendency for the malonate group to form a chelate ring is small.

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Part II

Thermodynamic Properties of Rare Earth Complexes.

XIV. Free Energy, Enthalpy and Entropy Changes for the Formation of Lanthanoid Malonate and Hydrogen Malonate Complexes.

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The changes in free energy, enthalpy and entropy for the formation of lanthanoid(III) malonate and hydrogen malonate complexes have been determined. The free energy changes were computed from the previously determined stability constants. The enthalpy changes were obtained from a direct calorimetric determination of the heats of complex formation. All data refer to a temperature of 25.0 °C and a sodium perchlorate medium with the sodium ion concentration equal to 1.00 M.

Earlier in this series of investigations on the thermodynamic properties of lanthanoid(III) carboxylate complexes, the stability constants for the formation of malonate and hydrogen malonate complexes have been determined¹. This paper describes a calorimetric determination of the corresponding enthalpy changes.

Values of the changes in free energy, entropy and enthalpy for the formation of the first malonate complex with lanthanum (3+), gadolinium(3+) and lutetium (3+) have been reported by Gelles and Nancollas². The enthalpy changes were determined from the temperature dependence of the stability constants; a method which will give enthalpy values with low precision.

Grenthe and Hansson have determined ΔG_j° , ΔH_j^c and ΔS_j° for the formation of scandium(III) malonate, diglycolate and dipicolinate complexes³. The values of the enthalpy change (ΔH_1°) and entropy change (ΔS_1°) for the formation of the first scandium diglycolate and dipicolinate complexes are of the expected magnitude, as estimated from the general trends in the variation of ΔH_1° and ΔS_1^c with respect to the ionic radius within the lanthanoid series. This is not the case for the entropy change for the formation of the second scandium diglycolate (and dipicolinate) complex.

The formation of the diglycolate and dipicolinate complexes is exothermic, while the formation of the malonate complexes is endothermic. The value of ΔS_1° is ^{about} the same for the formation of the malonate, diglycolate and dipicolinate complexes, whereas ΔS_2° for the malonate complex is much larger than for the other two complexes. With data for the corresponding lanthanoid complexes available, it might be possible to decide whether this "anomalous"

behaviour is due to the small radius of the scandium ion or to some property of the ligand.

The calorimeter described by Grenthe, Ots and Ginstруп⁴ has been used in this work. The measurements were performed at 25.00 °C in an aqueous sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M.

NOTATIONS AND CALCULATIONS

The notations used here have been defined in Refs. 1 and 5. The enthalpy changes have been calculated from the experimental data by the last-squares method "Letagrop Kalle", developed by Arnek and Sillén⁶. Only the heats of protonation of the malonate ion have been calculated by standard graphical methods⁷.

EXPERIMENTAL

Chemicals used. Stock solutions of the various rare earth perchlorates, malonic acid, disodium malonate and sodium perchlorate were prepared and analyzed as described before¹.

Procedure. The titration calorimeter developed by Grenthe et.al. was used for these measurements. Two different inner vessels have been used, one containing about 120 ml and the other about 103 ml. The inner vessel is filled with a solution S with an initial volume V_0 equal to 100.0 ml or 80.0 ml. When the S solution has the same temperature as the outer thermostat bath, a portion (at most 3 ml) of the titrant solution T is added from a piston burette. Additions were made at a constant rate, 1 ml/min.

When the inner vessel is filled, a suitable volume is withdrawn through the outlet tube, which is connected to a second piston burette.

The system is electrically calibrated, and in general two calibrations were made during each run.

The heats of dilution of the T solutions were determined by successive ^(additions) of T solution to an S solution consisting of 1.00 M NaClO_4 .

It was assumed that the heats of dilution of the metal ions and the various complexes could be neglected⁸.

The compositions of the S and T solutions have been chosen in order to cover a wide concentration range during the titrations. The different compositions are mainly of the following three types: The S solution contains only metal ion, while T is a solution with the ratio $\frac{C_H}{C_A}$ approximately equal to 1/1 (type I) or 1/3 (type II).

For type III, the S solution contains metal ion and perchloric acid (or malonic acid) and T is a buffer with the ratio $\frac{C_H}{C_A}$ less than 1/3.

Figures 1a and 1b show the concentration of the various species during titrations of the types II and III in the lutetium system. Titrations of type I give concentrations of the acid complexes intermediate to those in titrations of types II and III.

The formation of a slightly soluble compound of the composition $M_2A_3 \cdot nH_2O$ complicates the measurements. Thus, for the lighter elements (La-Tb), $\Delta H_{1,0,3}^{\circ}$ could not be determined and the precision in the determinations of $\Delta H_{1,0,1}^{\circ}$ and $\Delta H_{1,0,2}^{\circ}$ is low. In the potentiometric measurements some information on

$\beta_{1,0,3}$ could be obtained by making titration series "backwards", using an S solution with a high free ligand concentration and an acid titrator solution. This method can not be used in the calorimetric measurements, which are considerably more time-consuming than the potentiometric ones. A precipitate is formed in the S solution before the titration series is started.

RESULTS

The heat equivalent ϵ_V was the same for all the rare earths, and a linear relationship was established between ϵ_V and the total volume V of the system. The estimated maximum error in ϵ_V is $\pm 0.3\%$.

a. The proton-malonate system. The titrations were performed by adding perchloric acid to a solution of disodium malonate. The initial total concentrations of malonate ion were 50 mM and 100 mM, respectively.

Graphical calculation of the overall enthalpy changes for the formation of the two proton-malonate complexes gave the values:

$$\Delta H_{0,1,1}^{\circ} = (2.00 \pm 0.02) \text{ kJ/mol}$$

$$\Delta H_{0,2,1}^{\circ} = (0.46 \pm 0.02) \text{ kJ/mol}$$

(The errors are estimated maximum errors.) These values agree with those given in Ref. 3.

Using the stability constants in Ref.1, the following values are obtained for the changes in free energy and enthalpy for the formation of proton-malonate complexes at 25 °C:

$$\Delta G_{0,1,1}^{\circ} = (-28.90 \pm 0.02) \text{ kJ/mol}$$

$$\Delta G_{0,2,1}^{\circ} = (-43.68 \pm 0.04) \text{ kJ/mol}$$

$$\Delta S_{0,1,1}^{\circ} = (103.6 \pm 0.2) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta S_{0,2,1}^{\circ} = (148.0 \pm 0.2) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

b. The lanthanoid-malonate systems. The data for the lutetium malonate system are given in Table 1. The corrections for the dilution of the various titrator solutions have not been tabulated. These corrections are small and do not exceed 0.03 J/per ml added T solution.

The over-all enthalpy changes for the formation of the various complexes are given in Table 2. All values have been calculated by the least-squares procedure. Table 3 gives the corresponding free energy and entropy changes.

Table 2 also gives the standard deviation in the individual measurements, which has values of about 0.08 J. There are several sources for these errors, and some of them will be discussed.

i) An error of about 0.04 J in Q_{corr} can be attributed to errors in the calorimetric procedure, e.g. uncertainties in the graphical evaluation of the thermistor resistance change at the addition of titrant, and to temperature changes in the thermostat bath or in the calorimeter room during the measurements.

ii) The data in Table 1 show the presence of systematic errors in some titration series. If the enthalpy values are calculated for some of these series separately, results which differ slightly will be obtained. This is exemplified in Table 4, where data from Table 1 have been used.

The effects of concentration errors varies with the different types of compositions. The order of magnitude of these errors has been estimated for the various types of titrations. The figures given below refer to titrations performed with $(C_M)_S = 20 \text{ mM}$ and $(C_A)_T = 300 \text{ mM}$, which corresponds to the conditions for the lutetium and most of the other systems. Only concentration errors, which cause a great error in the measured heat, are discussed.

Type I. An error of 1 % in the ratio $(C_H/C_A)_T$ gives a corresponding change in Q_{corr} of 0.05 J/3 ml addition.

Type II. An error of 1 % in $(C_M)_S$ or $(C_A)_T$ each gives a change in Q_{corr} of about 0.04 J/3 ml addition.

Type III. An error of 1 % in $(C_A)_T$ gives a change in Q_{corr} of 0.10-0.04 J/3 ml addition.

iii) The heats of formation of the malonate complexes, which were determined in separate measurements, could be regarded as two additional unknown parameters to be determined from the measurements on the metal systems. When this was done in the ytterbium system, the following values were calculated

$$\Delta H_{0,1,1}^{\circ} = (1.80 \pm 0.25) \text{ kJ/mol}$$

$$\Delta H_{0,2,1}^{\circ} = (0.3 \pm 0.6) \text{ kJ/mol}$$

The other enthalpy values and the standard deviation in Q_{corr} remained ^{the} same. Thus, reasonable errors in $\Delta H_{0,1,1}^{\circ}$ and $\Delta H_{0,2,1}^{\circ}$ are without influence on the other enthalpy values.

iv) The complexes of the type MA_j are rather strong and the enthalpy values are thus not sensitive to errors in $\beta_{1,0,j}$. For the equilibrium $M + HA \rightleftharpoons MHA$ the equilibrium constant has a value about 20 M^{-1} , and the concentration of MHA thus strongly depends

on the value of $\beta_{1,1,1}$. Table 5 shows values of the error square sum $\underline{U}$ and $\underline{\Delta H}_{1,1,1}^O$, calculated for three different values of $\beta_{1,1,1}$, with data from the ytterbium system.

The shifts in $\beta_{1,1,1}$, which correspond to three standard deviations, have a very small effect on the error square sum. Only $\underline{Q}_{\text{corr}}$ -values from titrations series of the types I and III are affected, and this with 0.025 J at most. The changes in the concentration of the complex MHA are compensated by opposite concentration changes in MA, and as all the enthalpy values are of the same order or magnitude, the resulting change in $\underline{Q}_{\text{corr}}$ is small.

Calorimetric measurements on solutions with a low $\underline{C}_H/\underline{C}_A$ ratio can be described by the same set of "false" equilibrium constants that described the potentiometric measurements on this type of solutions, and a set of enthalpy values, which are nearly the same as the correct enthalpy values. The discussion in Ref. 1 showed that in these systems the erroneously calculated value of the concentration of free ligand, $\underline{a}^*$, is greatly in error, whereas the error in $\underline{n}^*$ is small. This means that the error in the concentration of MA is small. Thus, if the measurements had been performed by using only solutions with the ratio $\underline{C}_H/\underline{C}_A$ less than 1/2, neither the potentiometric nor the calorimetric measurements would have shown the existence of acid complexes in these solutions.

The calorimetric measurements do not give any check on the stability constants in these system.

DISCUSSION

The enthalpy and entropy changes of the complex formation reactions of lanthanoid ^{ions} with charged bases as ligands are often described by using a simple electrostatic model in connection with the Frank and Evans "iceberg" concept. Species in water solution are surrounded by a cloud of water molecules with a geometry different from that of the bulk water. The extension of this cloud depends on the size and charge of the central ion. As the complex formed has a greater radius and reduced charge as compared to the reactants, water molecules will be released in the association reaction. Thus, as regards the stepwise reactions, the entropy changes are expected to decrease in the order $\Delta S_1^0 > \Delta S_2^0 > \Delta S_3^0$. This is in accordance with experiments for the malonates and a number of other complexes⁹. The values in Table 3 also permits a calculation of the entropy changes for the reactions



and the expected relationship $\Delta S_{II}^0 > \Delta S_I^0$ is found.

Also, a ligand forming a chelate is expected to give a more positive entropy change than a unidentate ligand. The results for the reactions



for which $\Delta S_{III}^0 > \Delta S_{IV}^0$, are in accordance with this. As arguments based on radius and charge would have given the opposite relationship, this result indicates that malonate ion acts as a bidentate ligand. However, the model can not be used to make any quantitative estimates of the thermodynamic properties.

This same model also predicts that the function ΔH° vs $1/r$ (or ΔH° vs Z , as $1/r$ is an approximately linear function of Z for the lanthanoid ions), where r is the radius of the lanthanoid ion, should be linear. This is not the case, as is shown in Figure 2a for some examples. The similar shape of ΔH° vs Z plots (and also ΔS° vs Z) for the complex formation with many different ligands is an indication that the variation is due to some property of the metal ions, *i.e.* there is in the lanthanoid series a change of the structure of the solvation sphere or of the coordination number. A host of thermodynamic and other data have as yet not given any clear picture regarding these structural changes¹⁰⁻¹³. However, the thermodynamic investigation on diglycolate complexes by Grenthe and Ots¹⁴ gave evidence for the presence of a hydration equilibrium



for the second complex.

For the malonate complexes, the variation in $\Delta H^\circ_{1,0,1}$ is small (Fig 2b) and a plot of $\Delta S^\circ_{1,0,1}$ vs Z is approximately linear, increasing with decreasing metal ion size. The value of $\Delta H^\circ_{1,0,1}$ for the formation of the scandium complex is the same as for the heavy lanthanoids, whereas $\Delta S^\circ_{1,0,1}$ is about $30 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ more positive than one might expect from the value of the ionic radius of scandium. This behaviour might be compared with that of some other ligands of bidentate character, with oxygen as donator atoms.

Choppin and Friedman have determined the changes in free energy, enthalpy and entropy for the formation of lanthanoid lactate and α -hydroxyisobutyrate complexes¹⁵. The ΔH°_1 -values are negative and vary little across the lanthanoid series and the ΔS°_1 -values have

a small positive value, 15 to 40 J.K⁻¹.mol⁻¹, throughout the series. For the corresponding complexes with propionate and isobutyrate, respectively, the enthalpy changes are positive and the entropy changes are greater, 60 to 100 J.K⁻¹ mol⁻¹. An interpretation of this behaviour has been discussed by Grenthe¹⁶.

For the tropolonate systems¹⁷ a plot of ΔH_1^0 vs Z is given in Fig 2b. The behaviour of ΔS_1^0 vs Z is similar to that of the malonate systems. Campbell and Moeller propose, that a change in the hydration structure of the metal ions is compensated by a parallel structural change in the hydration spheres of the 1:1 complexes. This suggestion has as yet no experimental basis. In this connection, precise values of the thermodynamic parameters for the higher tropolonato complexes would be of interest. Due to experimental difficulties, these values have ^{not} been determined, neither for the malonate nor the tropolonate systems.

Entropy data for bidentate dicarboxylate complexes are scarce. One reason for this is the formation of sparingly soluble solids with this type of ligands. However, measurements on some maleinate systems are in progress at this laboratory and will be reported in a following publication.

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Table 1. Experimental results for the lutetium malonate system.

Corresponding values of $\underline{v}/\text{ml}$, $\underline{Q}_{\text{corr,exp}}/J$ and $(\underline{Q}_{\text{corr,calc}} - \underline{Q}_{\text{corr,exp}})/J$ are given. The withdrawal of solution from the inner vessel during a titration series is indicated by small letters, e.g. Series 1a,... Series 1b.

Series 1a. S: $\underline{C}_H = 0.05543 \text{ M}$, $\underline{C}_M = 0.01963 \text{ M}$, $\underline{C}_A = 0.02737 \text{ M}$,

$\underline{C}_{\text{NaClO}_4} = 1.000 \text{ M}$;

T: $\underline{C}_H = 0.1056 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.3018 \text{ M}$, $\underline{C}_{\text{NaClO}_4} = 0.502 \text{ M}$;

$\underline{V}_0 = 99.95 \text{ ml}$;

3.000, 4.050, -0.054; 6.000, 5.586, -0.264;

Series 1b. S: $\underline{C}_H = 0.05827 \text{ M}$, $\underline{C}_M = 0.01852 \text{ M}$, $\underline{C}_A = 0.04291 \text{ M}$,

$\underline{C}_{\text{NaClO}_4} = 0.972 \text{ M}$;

T: $\underline{C}_H = 0.1056 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.3018 \text{ M}$, $\underline{C}_{\text{NaClO}_4} = 0.502 \text{ M}$;

$\underline{V}_0 = 97.95 \text{ ml}$;

2.000, 3.799, -0.029; 4.000, 3.753, 0.004;

6.000, 3.607, 0.046; 8.000, 3.514, -0.021;

11.00, 4.975, -0.059; 14.00, 4.527, -0.004;

17.00, 4.146, 0.012;

Series 2. S: $\underline{C}_H = 0.05543 \text{ M}$; $\underline{C}_M = 0.01963 \text{ M}$, $\underline{C}_A = 0.02737 \text{ M}$,

$\underline{C}_{\text{NaClO}_4} = 1.000 \text{ M}$;

T: $\underline{C}_H = 0.1037 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.3016 \text{ M}$, $\underline{C}_{\text{NaClO}_4} = 0.500 \text{ M}$;

$\underline{V}_0 = 79.93 \text{ ml}$;

2.000, 2.531, 0.046; 4.000, 3.473, -0.033;

6.000, 3.807, -0.046; 8.000, 3.778, 0.017;

10.00, 3.686, -0.004; 12.00, 3.498, 0.004;

14.00, 3.289, 0.008; 16.00, 3.054, 0.038;

18.00, 2.866, 0.033; 20.00, 2.690, 0.021;

22.00, 2.468, 0.046;

Series 3. S: $\underline{C}_H = 0.000479 \text{ M}$, $\underline{C}_M = 0.01475 \text{ M}$, $\underline{C}_A = 0$,

$\underline{C}_{\text{NaClO}_4} = 1.000 \text{ M}$;

T: $\underline{C}_H = 0.05723 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.1953 \text{ M}$, $\underline{C}_{\text{NaClO}_4} = 0.667 \text{ M}$;

$\underline{V}_O = 100.00 \text{ ml}$.

3.000, 6.054, -0.079; 6.000, 5.887, -0.046;

9.000, 5.443, -0.046; 12.00, 4.678, 0.004;

15.00, 3.849, 0.025; 18.00, 3.117, 0.067;

Series 4. S: $\underline{C}_H = 0.000479 \text{ M}$, $\underline{C}_M = 0.01475 \text{ M}$, $\underline{C}_A = 0 \text{ M}$,

$\underline{C}_{\text{NaClO}_4} = 1.000 \text{ M}$;

T: $\underline{C}_H = 0.05723 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.1953 \text{ M}$, $\underline{C}_{\text{NaClO}_4} = 0.667 \text{ M}$;

$\underline{V}_O = 100.00 \text{ ml}$.

2.000, 3.958, 0.004; 5.000, 6.008, -0.067;

8.000, 5.623, -0.046; 11.00, 4.803, 0.142;

14.00, 4.071, 0.063; 17.00, 3.330, 0.071;

Series 5a. S: $\underline{C}_H = 0.001357 \text{ M}$, $\underline{C}_M = 0.007230 \text{ M}$, $\underline{C}_A = 0.003829 \text{ M}$,

$\underline{C}_{\text{NaClO}_4} = 0.994 \text{ M}$;

T: $\underline{C}_H = 0.05723 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.1953 \text{ M}$, $\underline{C}_{\text{NaClO}_4} = 0.667 \text{ M}$;

$\underline{V}_O = 102.00 \text{ ml}$.

3.000, 4.996, 0.251; 6.000, 4.012, -0.322;

9.000, 2.577, -0.197; 12.00, 1.669, -0.071;

15.00, 1.142, -0.025;

Series 5b. S: $\underline{C}_H = 0.00852 \text{ M}$, $\underline{C}_M = 0.006303 \text{ M}$, $\underline{C}_A = 0.02838 \text{ M}$,

$\underline{C}_{\text{NaClO}_4} = 0.952 \text{ M}$;

T: $\underline{C}_H = 0.05723 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.1953 \text{ M}$, $\underline{C}_{\text{NaClO}_4} = 0.667 \text{ M}$;

$\underline{V}_O = 100.00 \text{ ml}$.

3.000, 0.766, 0.038; 6.000, 0.548, 0.046;

9.000, 0.422, 0.038; 12.00, 0.402, -0.033;

15.00, 0.293, 0.008; 18.00, 0.213, 0.038;

Series 6. S: $\underline{C}_H = 0.000691 \text{ M}$, $\underline{C}_M = 0.01963 \text{ M}$, $\underline{C}_A = 0$,

$\underline{C}_{\text{NaClO}_4} = 1.000 \text{ M}$;

T: $\underline{C}_H = 0.3033 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.3024 \text{ M}$, $\underline{C}_{\text{NaClO}_4} = 0.698 \text{ M}$;

$\underline{V}_O = 79.93 \text{ ml}$.

2.000, 2.456, 0.117; 4.000, 1.966, 0.050;

6.000, 1.791, 0.042; 8.000, 1.607, 0.054;

10.00, 1.452, 0.067; 12.00, 1.289, 0.088;

14.00, 1.180, 0.067; 16.00, 1.063, 0.067;

18.00, 0.937, 0.084;

Series 7. S: $\underline{C}_H = 0.000691 \text{ M}$, $\underline{C}_M = 0.01963 \text{ M}$, $\underline{C}_A = 0$,

$\underline{C}_{\text{NaClO}_4} = 1.000 \text{ M}$;

T: $\underline{C}_H = 0.3033 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.3024 \text{ M}$, $\underline{C}_{\text{NaClO}_4} = 0.698 \text{ M}$;

$\underline{V}_O = 79.93 \text{ ml}$.

2.000, 2.456, 0.117; 4.000, 1.996, 0.021;

6.000, 1.807, 0.025; 8.000, 1.640, 0.022;

10.00, 1.477, 0.042;

Table 2. The over-all enthalpy values for the formation of lanthanoid malonate complexes.
The errors are equal to three standard deviations.

Metal ion	Number of experimental points	Standard deviation in $\bar{Q}_{\text{corr}}/\text{J}$	$\frac{\Delta H^{\circ}_{1,0,1}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta H^{\circ}_{1,0,2}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta H^{\circ}_{1,0,3}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta H^{\circ}_{1,1,1}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta H^{\circ}_{1,1,2}}{\text{kJ}\cdot\text{mol}^{-1}}$
La	29	0.082	12.1 $\pm$ 0.7	20.4 $\pm$ 2.6	-	5.2 $\pm$ 0.7	17.8 $\pm$ 1.7
Ce	31	0.082	12.2 $\pm$ 0.8	19 $\pm$ 10	-	5.3 $\pm$ 0.8	20.0 $\pm$ 2.5
Pr	39	0.111	12.7 $\pm$ 0.7	21.5 $\pm$ 1.8	-	5.3 $\pm$ 0.9	19.0 $\pm$ 4.2
Nd	33	0.086	13.1 $\pm$ 0.7	21.1 $\pm$ 3.3	-	5.0 $\pm$ 0.7	9.2 $\pm$ 2.2
Sm	43	0.094	12.5 $\pm$ 0.5	21.3 $\pm$ 2.0	-	5.6 $\pm$ 0.7	18.3 $\pm$ 1.4
Eu	42	0.085	12.8 $\pm$ 0.5	20.0 $\pm$ 3.8	-	5.9 $\pm$ 0.8	16.8 $\pm$ 1.0
Gd	47	0.087	12.6 $\pm$ 0.5	20.1 $\pm$ 2.1	-	6.5 $\pm$ 0.8	18.1 $\pm$ 1.5
Tb	42	0.072	12.61 $\pm$ 0.33	22.0 $\pm$ 0.7	-	7.6 $\pm$ 0.7	17.2 $\pm$ 0.8
Dy	49	0.086	12.83 $\pm$ 0.36	22.3 $\pm$ 0.9	23 $\pm$ 11	8.2 $\pm$ 1.2	18.0 $\pm$ 1.7
Ho	53	0.080	13.51 $\pm$ 0.32	22.1 $\pm$ 0.6	30 $\pm$ 2	6.9 $\pm$ 1.2	18.0 $\pm$ 1.2
Er	49	0.110	13.4 $\pm$ 0.5	22.5 $\pm$ 1.0	28 $\pm$ 11	6.3 $\pm$ 1.5	20.5 $\pm$ 2.0
Tm	52	0.077	14.46 $\pm$ 0.34	23.2 $\pm$ 0.5	33.9 $\pm$ 2.5	5.8 $\pm$ 1.8	17.0 $\pm$ 2.2
Yb	74	0.061	14.24 $\pm$ 0.20	24.40 $\pm$ 0.24	33.1 $\pm$ 0.9	7.9 $\pm$ 1.0	21.6 $\pm$ 1.6
Lu	57	0.091	14.59 $\pm$ 0.37	24.4 $\pm$ 0.6	35.2 $\pm$ 3.3	0.0 $\pm$ 1.5	24.6 $\pm$ 3.9

Table 3. $-\Delta G^\circ$ and ΔS° for the formation of lanthanoid malonate complexes at 25.0 °C.
(The entropy unit, $\text{J}\cdot\text{K}^{-1}\text{ mol}^{-1}$, is written e.u.)

Metal ion	$\frac{-\Delta G^\circ_{1,0,1}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{-\Delta G^\circ_{1,0,2}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{-\Delta G^\circ_{1,0,3}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{-\Delta G^\circ_{1,1,1}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{-\Delta G^\circ_{1,1,2}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta S^\circ_{1,0,1}}{\text{e.u.}}$	$\frac{\Delta S^\circ_{1,0,2}}{\text{e.u.}}$	$\frac{\Delta S^\circ_{1,0,3}}{\text{e.u.}}$	$\frac{\Delta S^\circ_{1,1,1}}{\text{e.u.}}$	$\frac{\Delta S^\circ_{1,1,2}}{\text{e.u.}}$
La	17.51	29.4	-	36.0	52.4	99	167	-	138	235
Ce	18.6	29.9	-	36.4	53.1	103	170	-	140	245
Pr	18.8	32	-	36.9	53	106	179	-	142	240
Nd	19.29	33.8	-	37.0	53.9	109	184	-	141	245
Sm	20.98	34.7	-	37.6	56.3	112	188	-	145	250
Eu	21.24	35.6	-	37.0	57.0	114	186	-	144	248
Gd	21.30	35.6	-	37.1	55.8	114	187	-	146	248
Tb	21.78	36.4	-	36.3	57.6	115	196	-	147	251
Dy	21.97	36.2	43	36.0	56.0	117	196	220	148	248
Ho	21.87	36.4	43.8	36.0	56.8	119	196	250	144	251
Er	21.98	36.5	43.5	36.2	56.7	119	198	240	143	259
Tm	21.95	36.7	43.5	35.8	57.0	122	201	260	140	248
Yb	22.09	36.6	44.4	35.5	55.7	122	205	260	146	259
Lu	22.14	36.6	45.0	35.7	54	123	208	269	147	260

Table 4. Enthalpy values for the lutetium malonate system, calculated from different titration series in Table 1.

Series used	Standard deviation in Q_{corr}/J	$\frac{\Delta H_{1,0,1}^{\circ}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta H_{1,0,2}^{\circ}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta H_{1,0,3}^{\circ}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta H_{1,1,1}^{\circ}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{\Delta H_{1,1,2}^{\circ}}{\text{kJ}\cdot\text{mol}^{-1}}$
1-7	0.0913	14.59 $\pm$ 0.37	25.4 $\pm$ 0.6	35.2 $\pm$ 3.3	8.0 $\pm$ 1.5	24.6 $\pm$ 3.9
1-5	0.0933	14.56 $\pm$ 0.38	25.5 $\pm$ 0.6	35.3 $\pm$ 3.4	8.9 $\pm$ 1.9	26.2 $\pm$ 4.5
3-7	0.0937	14.67 $\pm$ 0.40	25.6 $\pm$ 0.7	35.2 $\pm$ 3.4	7.1 $\pm$ 2.8	19.6 $\pm$ 8.7

Table 5. The error square sum U and $\Delta H_{1,1,1}^{\circ}$ calculated for three different values of $\beta_{1,1,1}$. The calculation refers to the ytterbium system with 74 experimental points.

$\frac{\beta_{1,1,1} \cdot 10^6}{\text{M}^{-2}}$	$\frac{\Delta H_{1,1,1}^{\circ}}{\text{kJ}\cdot\text{mol}^{-1}}$	$\frac{U}{\text{J}^2}$
1.41	8.4 $\pm$ 1.0	0.2715
1.63	8.1 $\pm$ 0.9	0.2673
1.85	7.8 $\pm$ 0.8	0.2666

Figure 1. The relative amounts of the different complexes in the lutetium malonate system during two titration series.

a Titration series of the type II. Data refer to series 5 a (lower volume scale) and 5 b (upper volume scale) in Table 1.

b Titration series of the type III, series 2 in Table 1.

Figure 2. The enthalpy changes for the formation of a. the first acetate¹⁶, diglycolate⁸ and EDTA¹⁸ lanthanoid complexes, and b. for the formation of the first malonate, hydrogen malonate and tropolonate¹⁷ complexes.

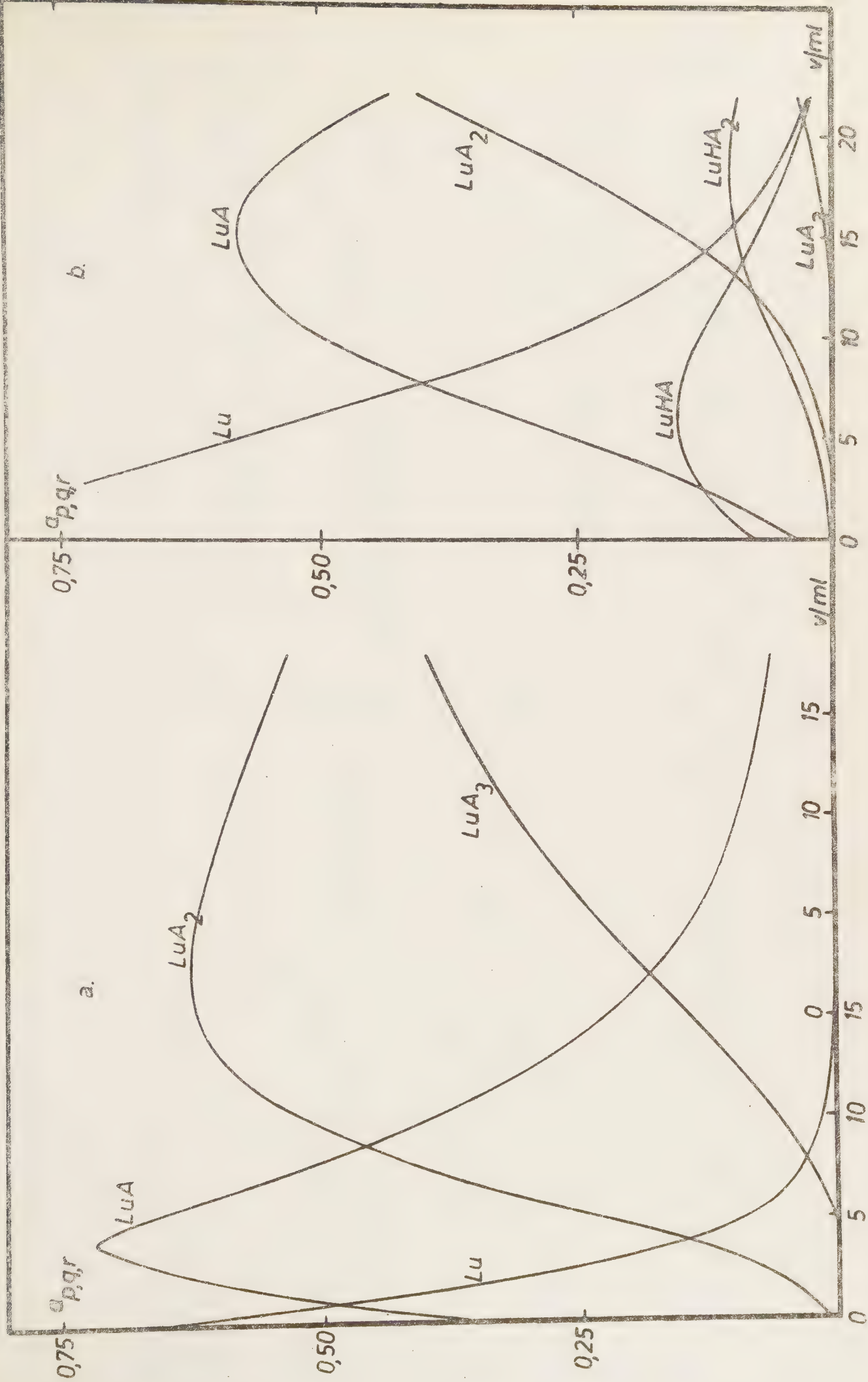
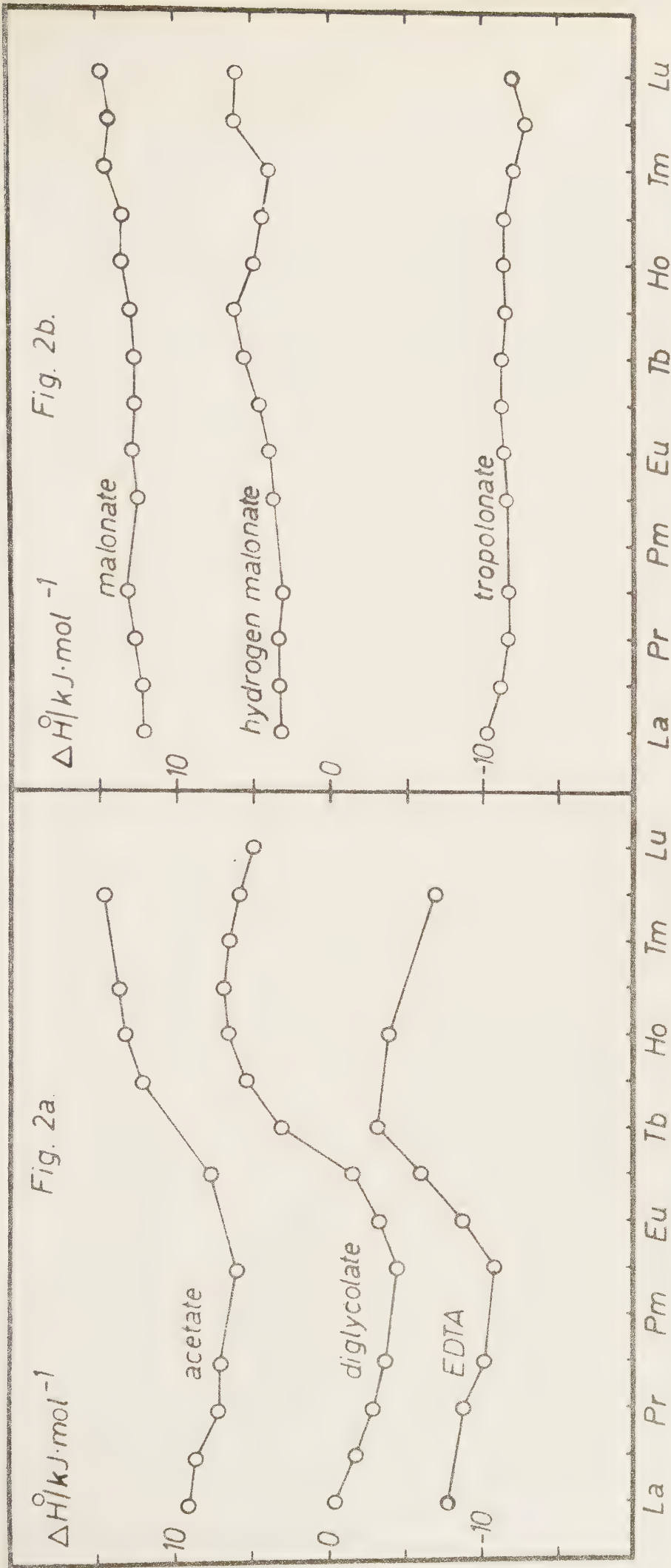


Figure 1.



Part III.

Thermodynamic Properties of Rare Earth Complexes.

XVIII. Free Energy, Enthalpy and Entropy Changes for the Formation of
Some Lanthanoid Thiodiacetate and Hydrogen Thiodiacetate Complexes.

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The changes in free energy, enthalpy and entropy for the formation of Ce, Pr, Sm, Tb, Er and Yb thiodiacetate and hydrogen thiodiacetate complexes with the compositions MA, MA₂, MHA and MHA₂ have been determined. The changes in free energy were calculated from stability constants, obtained from a potentiometric determination of the concentration of free hydrogen ion, using a glass electrode. The enthalpy values were measured calorimetrically. The measurements were performed at 25.0 °C in an aqueous sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M.

The possible formation of a complex MA₃ has been investigated in the praseodymium and ytterbium systems, using 4.00 M Na(ClO₄) as ionic medium.

The changes in thermodynamic functions such as ΔG_j° , ΔH_j° and ΔS_j° for the formation of lanthanoid(III)-complexes usually do not follow the monotonic dependence on the size of the metal ion as is suggested by simple electrostatic models of bonding. This non-monotonic size dependence is not a consequence of differences in electron configuration, as all the trivalent rare earth ions have a "noble gas" like configuration of the outer electron shells. Hence, one should try to base models which describe the observed size specificity in the complexation reactions on factors such as the size of the central ion, the geometrical requirements of the ligand, and the coordination of solvent molecules to the species participating in the complex formation reactions.

The coordinated donor atoms in the ligands may be described as forming a cavity, the size of which depends on the size of the central ion and the way in which the donor atoms are interconnected in the ligand. In general, one must expect that a coordinated ligand can not be arranged as freely as the solvent molecules in the coordination shell. Hence, the cavities formed by the coordinated donor atoms in multidentate ligands can not be expected to contract to the same extent as the cavities formed by the coordinated solvent molecules as the size of the metal ion decreases. The resulting differences in the geometry of the coordination spheres will give rise to a size specificity in the complexation reactions.

In previous parts of this series we have reported thermodynamic data for complexation reactions in aqueous solution between rare earths and the ter-dentate ligands 2,6-pyridinedicarboxylate (= dipicolinate¹), imino-diacetate² and oxydiacetate³. They all form stable chelates with a maximum of three ligands coordinated in each case, presumably giving rise to nine-coordinated complexes in solution. The variations through the rare earth

series of the thermodynamic quantities are also very similar, e.g. the pronounced difficulty for the third complex to be formed for the central ions with the smallest ionic radius. The observed similarities are probably due to a similar coordination geometry for the three ligands, as judged from the structures of solids containing the complexes^{4,5}.

We have extended the previous investigations to include the ter--dentate ligand thiodiacetate, which contains a sulphur atom as the third donor atom. As the rare earths are typical a-acceptors and thus have a much smaller affinity to sulphur than to nitrogen and oxygen, a substantial decrease in stability is expected for the thiodiacetate complexes as compared to those with nitrogen and oxygen donors.

The radius of the sulphur atom is about 30 % larger than the radii of nitrogen and oxygen. Sulphur atoms in the equatorial plane of a tri-capped trigonal prism, which is the most common coordination polyhedron in solid rare earth complexes are, because of their size, expected to be closer to one another than the equatorial atoms in the dipicolinate, iminodiacetate and oxydiacetate complexes. Thus, purely geometrical constraints might give an additional decrease in stability for the higher thiodiacetate complexes.

In systems containing polyprotic acids and their conjugate bases, the possibility of complex formation with all these various ligands must be kept in mind. This will lead to an increased difficulty in the interpretation of the experimental data, especially when the concentration of free ligand can not be measured directly. Acid complexes have been found only for the iminodiacetate systems², a fact that undoubtedly is due to the high basicity of iminodiacetate as compared to the other ligands. Thiodiacetate has very nearly the same base strength as oxydiacetate. On the other hand, the expected decrease in stability of the thiodiacetate complexes ought to increase the possibility for acid complexes to appear in noticeable amounts.

4.

Because of the similarity in geometry of oxydiacetate, iminodiacetate, dipicolinate and thiodiacetate, it is expected that they will interact in a similar way with a given lanthanoid ion. The pronounced similarities in the variations of the ΔH_j^0 and ΔS_j^0 values through the lanthanoid series for the oxydiacetate, iminodiacetate and dipicolinate complexes can thus be expected to include also the thiodiacetate complexes.

This study of lanthanoid thiodiacetates has been undertaken mainly in order to obtain quantitative information about the coordinating ability of various donors in rare earth complexes of similar geometry. Measurements have been performed in solutions with a high concentration of hydrogen thiodiacetate ion in order to get information concerning the formation of acid complexes. The changes in ΔG_j^0 , ΔH_j^0 and ΔS_j^0 have been determined for six lanthanoid ions, viz. Ce^{3+} , Pr^{3+} , Sm^{3+} , Tb^{3+} , Er^{3+} and Yb^{3+} , which should give sufficient information on the variation pattern of these properties across the lanthanoid series. The stability constants have been calculated from potentiometric determinations of the concentration of free hydrogen ion by means of a glass electrode. The various heats of complexation have been determined calorimetrically. Most data refer to a temperature of 25.0 °C and an aqueous sodium perchlorate medium with the sodium ion concentration equal to 1.00 M. However, in order to obtain the possible formation of information on a third complex, accurate experimental data at high ligand concentrations are needed. This is not easy, as changes in the composition of the medium will cause changes in the activity coefficients of the reacting species and/or the appearance of diffusion potentials in the emf measurements. In order to minimize these effects and get as accurate emf-data as possible, even at high concentrations of the ligand, stability constants for the praseodymium and ytterbium systems have also been measured in 4.00 M $NaClO_4$.

NOTATIONS AND CALCULATIONS

The notations have been defined previously^{2,8}.

The stability constants and enthalpy values have been calculated from the experimentally determined values of ($\bar{y}/\text{ml}$, E/mV) and ($\bar{y}/\text{ml}$, Q_{corr}/J), respectively, by the least-squares procedures "Etiter" and "Kalle" in the "Letagrop" series^{6,7}. The proton thiodiacetate system has also been treated with standard graphical procedures.

EXPERIMENTAL

Chemicals used. A stock solution of cerium perchlorate was prepared by dissolving cerium(III)nitrate (BDH, 99 %) in perchloric acid, precipitating the cerium as carbonate and redissolving the precipitate in perchloric acid. The other metal perchlorate solutions were prepared and analyzed as described before⁸. Thiodiacetic acid (Schuchard, 96 %) was purified with active charcoal and recrystallized twice from water. The purity was checked by alkalimetric titration and the formula weight was found to be 150.4 (calcd. 150.1).

The various buffers were obtained by mixing the appropriate amounts of solutions of thiodiacetic acid and sodium hydroxide. The sodium ion concentration was adjusted to 1.00 M (or 4.00 M, respectively) by addition of sodium perchlorate solution.

Potentiometric measurements. The equipment and experimental procedure in the potentiometric measurements were the same as described earlier⁸.

The protonation constants of the thiodiacetate ion were determined in solutions with $\bar{C}_M = 0$ and with different, constant values of $\bar{C}_A$. In 1 M $\text{Na}(\text{ClO}_4)$, these values of $\bar{C}_A$ were equal to 20 mM, 40 mM and 100 mM,

respectively. For the corresponding measurements in 4 M $\text{Na}(\text{ClO}_4)$, the $\underline{C}_A$ -values were 50 mM, 100 mM and 200 mM, respectively.

About six titration series have been made on each of the lanthanoid thiodiacetate systems, using solutions with different compositions. A wide concentration range with respect to thiodiacetate and hydrogen thiodiacetate ion must be covered in order to get solutions containing measurable amounts of the various complexes. The ratio $\underline{C}_H/\underline{C}_A$ in the different solutions varied from 2 to 1/10, and the total metal ion concentration varied from 8 mM to 35 mM. Table 1 shows the compositions of the solutions used for the measurements on the terbium system.

For the measurements in 4 M $\text{Na}(\text{ClO}_4)$, only one buffer solution with the ratio $\underline{C}_M/\underline{C}_A$ equal to 1/5 was used, and three titration series were made for each system. A precipitate with the composition $\text{M}_2\text{A}_2 \cdot n\text{H}_2\text{O}$ is formed during the titration, but it was dissolved if T solution was added in excess at once.

Calorimetric measurements. The measurements were performed as titrations in the same way as described earlier⁹.

The heats of protonation of thiodiacetate ion were determined by titrating a disodium thiodiacetate solution with perchloric acid.

In order to determine the enthalpies of formation of the various lanthanoid-thiodiacetate complexes, titration series have been made with solutions of the following types:

Metal perchlorate solutions were titrated with thiodiacetate buffers with the ratio $\underline{C}_H/\underline{C}_A$ equal to 1 or 1/4. In the third type of titration, a hydrogen thiodiacetate solution was titrated with a metal perchlorate solution.

The different solutions used for the measurements on the terbium system are given in Table 2. Most of the titrations were repeated once.

The heats of dilution of the various T solutions were determined in separate experiments and were found to be negligible.

RESULTS

Determination of the stability constants.

Measurements in 1 M Na(ClO₄). A least-squares treatment of ($\bar{n}_H$, h)-data gave the following values of the two protonation constants of the thiodiacetate ion.

$$\beta_{0,1,1} = (9.84 \pm 0.10) \cdot 10^3 \text{ M}^{-1}$$

$$\beta_{0,2,1} = (1.34 \pm 0.01) \cdot 10^7 \text{ M}^{-2}$$

(The errors given above and in the following are equal to three standard deviations). The standard deviation in $\bar{n}_H$ was equal to $2.7 \cdot 10^{-3}$, and 102 experimental points were used in the calculation.

The constants vary somewhat with C_A ; $\beta_{0,1,1}$ thus increases with approx. 1 % as C_A is increased from 20 mM to 40 mM. This variation might be caused by an uncompensated liquid junction potential.

Some experimental values of $\bar{n}^*$ vs. $-\log(a^*/M)$ for the praseodymium thiodiacetate system are shown in Figure 1 (a). The fact that different curves are obtained in titrations with different values of the ratio C_H/C_A , clearly indicates that complexes of the composition $M \underset{p}{H} \underset{q}{A} \underset{r}{A}$ with $q > 0$ are formed.

The curves obtained at C_M equal to 19 mM and 35 mM are very nearly the same, indicating that polynuclear species are not formed in appreciable amounts. Since the highest value of $\bar{n}^*$ is 1.4, complexes with at least two ligands per metal ion must be formed, but no conclusions can be drawn about the existence of a third complex.

It is not possible in these systems to determine directly from experimental data the stoichiometry of the complexes formed; neither can standard graphical procedures be used. Instead, the results of using different "probable" models have been calculated.

In the first model, which was based on the results presented in Figure 1 (a) the following assumptions were made:

- i. Two binary complexes with the compositions MA and MA₂ are formed.
- ii. One acid complex, viz. MHA, is formed.
- iii. Polynuclear species are not formed.

The calculated stability constants were positive and the standard deviation in $\frac{C_H}{C_A}$ was equal to $7.75 \cdot 10^{-3}$. (The figures refer to the terbium system).

There is no reason to include the complex MA₃ in the calculations, (possible) but the presence of other acid complexes, viz. MHA₂ or MH₂A₂, has been investigated. The results are:

$$\beta_{1,1,2} = (1.98 \pm 0.36) \cdot 10^7 \text{ M}^{-3}; \text{ sig } \frac{C_H}{C_A} = 4.48 \cdot 10^{-3}$$

$$\beta_{1,2,2} = (2.3 \pm 0.8) \cdot 10^9 \text{ M}^{-4}; \text{ sig } \frac{C_H}{C_A} = 6.90 \cdot 10^{-3}$$

From these values of the stability constants, it is found that $\alpha_{1,1,2}$ amounts to 0.05-0.10 in some solutions, while $\alpha_{1,2,2}$ is always less than 0.01 in the solutions studied.

(possible presence of)
The binuclear complexes M₂A and M₂HA has also been studied. These species did not improve the over-all description of the experimental data, i.e. the standard deviation in $\frac{C_H}{C_A}$ was not lowered and the corresponding stability constants were zero or negative.

Thus, it can be concluded that the species MH₂A₂, M₂A and M₂HA₂ are not present in any significant amounts, if at all, in the solutions studied.

From the experimental data, stability constants for the formation of the complexes MA , MA_2 , MHA and MHA_2 have been calculated. The stability constants with their estimated errors are given in Table 3. Some of the experimental data for the terbium system are given in Table 1.

It is assumed that the values of the protonation constants remain the same when $\underline{C}_M \neq 0$ as when $\underline{C}_M = 0$. This assumption was tested for the terbium system. When the protonation constants were varied with the other constants, the standard deviation in $\underline{C}_H/\underline{C}_A$ was lowered from $4.48 \cdot 10^{-3}$ to $4.01 \cdot 10^{-3}$, but the constants calculated in this way agreed, within the limits of error, with those given in Table 3. It can be concluded that any systematic variation of the protonation constants with $\underline{C}_M$ and $\underline{C}_A$ is less than the error limits given.

Measurements in 4 M Na(ClO₄). The protonation constants of the ligand must be accurately known if reliable values of $\bar{n}$ and $\underline{a}$ are to be obtained. Table 4 shows the protonation constants, calculated for each experimental $\underline{C}_A$ -value separately. The increase in $\beta_{0,1,1}$ with $\underline{C}_A$ must be taken into account in the calculation of the stability constants.

For each of the praseodymium and ytterbium systems, about 30 experimental points were determined. If the presence of acid complexes is neglected in the calculations, the calculated values of the concentration of free ligand, $\underline{a}$, and the ligand number, $\bar{n}$, are incorrect and will be denoted $\underline{a}^*$ and $\bar{n}^*$, respectively (cf. ref. 8). From these $(\bar{n}^*, \underline{a}^*)$ -values erroneous "stability constants", β_j^* , are obtained, which are smaller than the true constants. However, the ratio $\beta_j^{*2}/(\beta_{j+1}^* \cdot \beta_{j-1}^*)$ should give a good estimate of the ratio of the stepwise stability constants, $\underline{K}_j/\underline{K}_{j+1}$. Hence, we have estimated the magnitude of the ratio $\underline{K}_2/\underline{K}_3$ from the experimental $(\bar{n}^*, \underline{a}^*)$ -values. For each titration series, two sets of $(\bar{n}^*, \underline{a}^*)$ -values have been calculated, using two different values of $\beta_{0,1,1}$. These values correspond to the smallest and largest value of $\underline{C}_A$, respectively, which were used during the titration in the region where $\bar{n}^*$ is greater than

1.6. From the "upper limit" of $(\bar{n}^*, \underline{a}^*)$ -values thus obtained, the lower limit of the ratio K_2/K_3 is estimated. For the praseodymium system, experimental values of $(\bar{n}^*, -\log \underline{a}^*/M)$ are shown in Figure 1 (b), together with the $\bar{n}^*$ vs. $-\log (\underline{a}^*/M)$ curve from which the lower limit of K_2/K_3 has been estimated. The ytterbium system was treated in a similar way. Table 5 gives the results and a comparison with the values obtained in 1 M $\text{Na}(\text{ClO}_4)$.

A "Letagrop" calculation with the acid complexes included gave the same value of K_2/K_3 as the procedure described above.

Determination of the enthalpy values.

The following values for the heats of protonation of the thiodiacetate ion were obtained:

$$\underline{\Delta H}_{0,1,1}^{\circ} = (1.82 \pm 0.11) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\underline{\Delta H}_{0,2,1}^{\circ} = (1.36 \pm 0.15) \text{ kJ} \cdot \text{mol}^{-1}$$

The standard deviation in $\underline{Q}_{\text{corr}}$ was 0.10 J and 19 experimental points were measured.

The changes in free energy and entropy for the formation of the proton-thiodiacetate complexes at 25.0 °C are:

$$\underline{\Delta G}_{0,1,1}^{\circ} = (-22.79 \pm 0.02) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\underline{\Delta G}_{0,2,1}^{\circ} = (-40.68 \pm 0.02) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\underline{\Delta S}_{0,1,1}^{\circ} = (82.5 \pm 0.4) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\underline{\Delta S}_{0,2,1}^{\circ} = (140.9 \pm 0.6) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

The heats of formation of the various rare earth thiodiacetate complexes, calculated with the least-squares procedure, are given in Table 6. The standard deviations in the individual measurements, $\underline{\text{sig}} \underline{Q}_{\text{corr}}$, are of the magnitude expected from the precision of the calorimetric equipment.

DISCUSSION

The stability constants for the lanthanoid thiodiacetate complexes are considerably smaller than those for the corresponding oxydiacetate³, dipicolinate¹ or iminodiacetate² complexes. In the oxydiacetate complexes, two five-membered chelate rings are formed, which makes these complexes stronger than the corresponding oxalate complexes. The thiodiacetate complexes are even weaker than those formed with the bidentate malonate ion⁸. One can thus safely conclude that sulphur is a much poorer donor than oxygen in this case.

For the oxydiacetates and dipicolinates there is an increased difficulty for the third complex to be formed as the ionic radius of the lanthanoid decreases, as judged from the variation of the ratio K_2/K_3 of the stepwise stability constants. This ratio increases from 30 for the light lanthanoids to more than 100 for ytterbium and lutetium. Scandium does not form any third complex at all with these ligands. A comparison with the thiodiacetates is made difficult by the experimental problems in determining the stability constants of a third complex. However, the values given above show that the ratio K_2/K_3 is larger than 60 for the thiodiacetates, i.e. it is indeed difficult for the third complex to be formed. The values of the ratio K_1/K_2 are about 10, which shows that there is no problem in forming the second complex. This ratio has also very nearly the same value as for the corresponding oxydiacetates. These findings indicate that the larger radius of the sulphur atom makes the formation of a third thiodiacetate complex difficult even for the lanthanoid ions with the largest ionic radii. The magnitude of the stepwise stability constant K_3 is small. This indicates that the ligand in the third complex, if this complex is formed at all, is bounded only to one carboxylate group.

The stability constants for the complexation with the protonated ligand, i.e. $M + HA \rightleftharpoons MHA$, are in the range $12-40 \text{ M}^{-1}$ for the thiodiacetates, which is of the same order of magnitude as for the malonates⁸. For the hydrogen malonates, the strength of the acid MHA increases when the metal ion becomes smaller. This was described as due to an increased electrostatic repulsion between the central ion and the bonded proton when the size of the metal ion decreased. A similar result is not found for the hydrogen thiodiacetates, for which pK_a for MHA is roughly constant through the rare earth series. The larger distance between the carboxylate groups in the thiodiacetate ion, as compared with the malonate ion might be an explanation for this finding.

The low stability of the thiodiacetates is mainly an enthalpy effect, whereas the entropy term is of the same order of magnitude as for the oxydiacetates. The variation pattern of the functions ΔH_1^0 vs Z and ΔS_1^0 vs Z are very similar for the thiodiacetates, oxydiacetates¹⁰, dipicolinates¹⁰ and iminodiacetates². It is reasonable to assume that these geometrically similar dicarboxylate ligands cause approximately the same changes in the hydration shell of a given metal ion, at least on the formation of the first complex. This will roughly account for the similarities in the entropy changes.

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Table 1. Experimental results of the potentiometric measurements on the terbium system. The results are given as v/ml, $\underline{E}$ /mV, $\bar{n}_H$, $(\bar{n}_{H,calc} - \bar{n}_{H,exp})10^3$. The sodium ion concentration is 1.00 M in all solutions. Approximately one half of the experimental data are given.

Series 1. S: $\underline{C}_H = 0.00068$ M, $\underline{C}_M = 0.03184$ M, $\underline{C}_A = 0$;

T: $\underline{C}_H = 0.06098$ M, $\underline{C}_M = 0$, $\underline{C}_A = 0.1906$ M;

$\underline{V}_O = 20.00$ ml, $\underline{E}_O = 361.1$ mV.

0.900, 147.9, 0.369, 1.21; 1.400, 145.3, 0.353, 2.53; 2.500, 141.1, 0.341, 5.42; 3.900, 136.4, 0.333, 6.80; 5.300, 132.1, 0.330, 6.80; 6.800, 127.9, 0.328, 4.65; 8.500, 123.9, 0.327, 1.97; 10.60, 120.1, 0.325, -0.18; 13.60, 116.0, 0.324, -4.47; 17.00, 112.9, 0.323, -7.46; 22.00, 109.8, 0.322, -10.88; 28.00, 107.6, 0.322, -14.32; 35.00, 105.9, 0.322, -16.89;

Series 2. S: $\underline{C}_H = 0.05061$, $\underline{C}_M = 0.01990$, $\underline{C}_A = 0.02509$ M;

T: $\underline{C}_H = 0.00064$, $\underline{C}_M = 0.01990$ M, $\underline{C}_A = 0.05018$ M;

$\underline{V}_O = 20.00$ ml, $\underline{E}_O = 361.5$ mV.

0.0, 226.1, 1.812, -1.18; 0.400, 221.2, 1.774, -1.19; 0.800, 216.6, 1.732, -1.77; 1.300, 211.5, 1.677, -1.22; 1.800, 206.9, 1.622, -2.70; 2.500, 201.5, 1.545, -2.63; 3.200, 196.9, 1.473, -3.28; 4.100, 191.9, 1.388, -4.16; 5.200, 186.8, 1.295, -5.02; 6.500, 181.8, 1.198, -5.09; 8.000, 177.0, 1.103, -5.90; 10.00, 171.6, 0.997, -3.12; 12.10, 166.8, 0.905, -2.64; 14.60, 161.9, 0.816, -2.45; 17.70, 156.8, 0.727, -0.83; 21.20, 151.8, 0.646, -1.05; 25.40, 146.8, 0.574, 0.48; 30.20, 141.9, 0.507, 1.14; 36.00, 136.0, 0.445, 1.88;

Series 3. S: $\underline{C}_H = 0.1405 \text{ M}$, $\underline{C}_M = 0.01990 \text{ M}$, $\underline{C}_A = 0.07005 \text{ M}$;

T: $\underline{C}_H = 0.00064 \text{ M}$, $\underline{C}_M = 0.01990 \text{ M}$, $\underline{C}_A = 0.05018 \text{ M}$;

$\underline{V}_O = 20.00 \text{ ml}$, $\underline{E}_O = 361.5 \text{ mV}$.

0.0, 234.7, 1.865, 0.02; 0.600, 229.3, 1.834, 0.46; 1.150, 224.7, 1.803,
0.77; 1.800, 219.8, 1.764, 1.30; 2.550, 214.8, 1.717, 1.44; 3.400, 209.9,
1.664, 1.27; 4.400, 205.0, 1.603, 1.09; 5.600, 200.0, 0.07; 7.100, 194.9,
1.455, 0.82; 8.800, 189.9, 1.373, -1.58; 10.90, 184.9, 1.284, -0.95; 13.40,
179.9, 1.191, -0.49; 16.40, 174.8, 1.095, -1.11; 20.00, 169.6, 0.999, -2.60;
24.00, 164.9, 0.910, -0.27; 29.00, 159.8, 0.819, -0.02; 35.20, 154.5, 0.729,
0.52;

Table 2. Experimental results of the calorimetric measurements on the terbium system. Corresponding values of $\underline{v}/\text{ml}$, $\underline{Q}_{\text{corr,exp}}/\text{J}$ and $(\underline{Q}_{\text{corr,calc}} - \underline{Q}_{\text{corr,exp}}) \cdot 10^3/\text{J}$ are given. The sodium ion concentration is 1.00 M in all solutions.

Series 1. S: $\underline{C}_H = 0.000417 \text{ M}$, $\underline{C}_M = 0.02023 \text{ M}$, $\underline{C}_A = 0$;

T: $\underline{C}_H = 0.05870 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.2660 \text{ M}$;

$\underline{V}_O = 79.98 \text{ ml}$.

1.000, 3.008, 50; 3.000, 5.886, 16; 5.000, 5.112, 12; 7.000, 4.326, -46;
9.000, 3.518, -42; 11.00, 2.824, -46; 13.00, 2.255, -42; 15.00, 1.585, 181;
17.00, 1.426, -8; 19.00, 1.100, 55;

Series 2. S: $\underline{C}_H = 0.000417 \text{ M}$, $\underline{C}_M = 0.02023 \text{ M}$, $\underline{C}_A = 0$;

T: $\underline{C}_H = 0.05870 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.2660 \text{ M}$;

$\underline{V}_O = 79.98 \text{ ml}$.

2.000, 6.054, 46; 4.000, 5.497, 29; 6.000, 4.723, -12; 8.000, 3.945, -76;
10.00, 5.150, -34; 12.00, 2.531, -55; 14.00, 1.995, -20; 16.00, 1.548, 29;
18.00, 1.246, 29; 20.00, 1.033, 12;

Series 3. S: $\underline{C}_H = 0.2441 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.2374 \text{ M}$;

T: $\underline{C}_H = 0.000417 \text{ M}$, $\underline{C}_M = 0.02023 \text{ M}$, $\underline{C}_A = 0$;

$\underline{V}_O = 79.98 \text{ ml}$.

1.000, 0.397, 16; 3.000, 0.790, 29; 5.000, 0.811, 4; 7.000, 0.803, 8;
9.000, 0.820, -16; 11.00, 0.774, 20; 13.00, 0.782, 4; 15.00, 0.799, -16;
17.00, 0.765, 8; 19.00, 0.761, 8;

Series 4. S: $\underline{C}_H = 0.2441 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.2374 \text{ M}$;

T: $\underline{C}_H = 0.000417 \text{ M}$, $\underline{C}_M = 0.02023 \text{ M}$, $\underline{C}_A = 0$;

$\underline{V}_O = 79.98 \text{ ml}$.

2.000, 0.832, -8; 4.000, 0.811, 8; 6.000, 0.824, -12; 8.000, 0.815, -8;
10.00, 0.757, 41; 12.00, 0.807, -12; 14.00, 0.794, -8; 16.00, 0.753, 25;
18.00, 0.728, 41; 20.00, 0.728, 37;

Series 5. S: $\underline{C}_H = 0.000417 \text{ M}$, $\underline{C}_M = 0.02023 \text{ M}$, $\underline{C}_A = 0$;

T: $\underline{C}_H = 0.2441 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.2374 \text{ M}$;

$\underline{V}_O = 79.98 \text{ ml}$.

3.000, 3.631, -25; 5.000, 2.096, 0; 7.000, 2.058, -134; 9.000, 1.962, -205;
11.00, 1.594, 4; 13.00, 1.489, -29; 15.00, 1.347, -20; 17.00, 1.171, 29;
19.00, 1.117, -25;

Series 6. S: $\underline{C}_H = 0.000417 \text{ M}$, $\underline{C}_M = 0.02023 \text{ M}$, $\underline{C}_A = 0$;

T: $\underline{C}_H = 0.2441 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.2374 \text{ M}$;

$\underline{V}_O = 79.98 \text{ ml}$.

2.000, 2.464, 71; 4.000, 2.196, -4; 6.000, 1.987, 25; 8.000, 1.849, -12;
10.00, 1.707, -33; 12.00, 1.460, 64; 14.00, 1.384, 4; 16.00, 1.280, -16;
18.00, 1.167, -20;

Table 3. Stability constants for the lanthanoid thiodiacetate systems studied. The errors are equal to three standard deviations.

Metal ion	Number of points	$\frac{\text{sig } C_H}{C_A}$	$\beta_{1,0,1} \cdot 10^{-2} \cdot M$	$\beta_{1,0,2} \cdot 10^{-4} \cdot M^2$	$\beta_{1,1,1} \cdot 10^{-5} M^2$	$\beta_{1,1,2} \cdot 10^{-7} \cdot M^3$
Ce	92	$6.08 \cdot 10^{-3}$	4.53 ± 0.11	3.07 ± 0.22	2.30 ± 0.24	4.6 ± 1.2
Pr	140	$5.08 \cdot 10^{-3}$	5.55 ± 0.17	2.43 ± 0.17	2.81 ± 0.21	4.4 ± 0.9
Sm	169	$4.56 \cdot 10^{-3}$	8.01 ± 0.31	4.80 ± 0.24	3.91 ± 0.23	6.6 ± 1.3
Tb	110	$4.48 \cdot 10^{-3}$	3.30 ± 0.06	1.33 ± 0.06	1.61 ± 0.11	1.98 ± 0.36
Er	120	$4.07 \cdot 10^{-3}$	2.30 ± 0.030	0.704 ± 0.030	1.38 ± 0.07	1.61 ± 0.22
Yb	120	$5.56 \cdot 10^{-3}$	2.30 ± 0.037	0.576 ± 0.038	1.25 ± 0.10	1.87 ± 0.30

Table 4. The protonation constants of thiodiacetate ion in 4.00 M Na(ClO₄), calculated for each experimental $\underline{C}_A$ -value separately.

$\frac{\underline{C}_A}{\text{mM}}$	Number of points	$\beta_{0,1,1} \cdot 10^4 \cdot \text{M}$	$\beta_{0,2,1} \cdot 10^{-8} \cdot \text{M}^2$	$\text{sig } (\underline{C}_H / \underline{C}_A)$
50	69	3.66 ± 0.014	1.664 ± 0.010	$1.37 \cdot 10^{-3}$
100	76	3.74 ± 0.012	1.668 ± 0.006	$0.99 \cdot 10^{-3}$
200	77	3.95 ± 0.011	1.784 ± 0.006	$1.02 \cdot 10^{-3}$

Table 5. Stability constants for the formation of the non-acid complexes MA_4 and the ratios of the stepwise stability constants, determined in 1 M $Na(ClO_4)$ and 4 M $Na(ClO_4)$, respectively.

Metal ion	Medium:							
	1.00 M $Na(ClO_4)$				4.00 M $Na(ClO_4)$			
	$\beta_{1,0,1} \cdot M$	$\beta_{1,0,2} \cdot M^2$	K_1/K_2	$\beta_{1,0,1} \cdot M$	$\beta_{1,0,2} \cdot M^2$	$\beta_{1,0,3} \cdot M^3$	K_1^*/K_2^*	K_2^*/K_3^*
Pr	$5.55 \cdot 10^2$	$2.43 \cdot 10^4$	12.7	$1.10 \cdot 10^3$	$1.4 \cdot 10^5$	$3 \cdot 10^5$	8.7	60
Yb	$2.296 \cdot 10^2$	$5.76 \cdot 10^3$	9.2	$7.0 \cdot 10^3$	$5.4 \cdot 10^4$	$8 \cdot 10^4$	9.1	51

Table 6. The overall values of ΔH° , ΔG° and ΔS° for the lanthanoid thiodiacetate systems studied. The enthalpy values are tabulated with their estimated maximum errors, equal to three standard deviations. The standard deviation $\text{sig } Q_{\text{corr}}$ in the measured Q_{corr} values and the number of experimental points in the calorimetric titrations are also given. The ΔH° and ΔG° -values have been divided with $\text{kJ}\cdot\text{mol}^{-1}$, the ΔS° -values with $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.

	Ce	Pr	Sm	Tb	Er	Yb
$\Delta H_{1,0,1}^\circ$	12.80 $\pm$ 0.29	12.16 $\pm$ 0.45	11.38 $\pm$ 0.12	17.20 $\pm$ 0.39	20.96 $\pm$ 0.33	22.38 $\pm$ 0.18
$\Delta G_{1,0,1}^\circ$	-15.15	-15.65	-16.57	-14.39	-13.47	-13.47
$\Delta S_{1,0,1}^\circ$	93.7	93.3	93.7	105.9	115.5	120.1
$\Delta H_{1,0,2}^\circ$	20.29 $\pm$ 0.45	19.7 $\pm$ 1.1	20.63 $\pm$ 0.24	26.3 $\pm$ 0.8	33.1 $\pm$ 0.8	36.1 $\pm$ 0.5
$\Delta G_{1,0,2}^\circ$	-25.61	-19.66	-26.69	-23.56	-21.97	-21.46
$\Delta S_{1,0,2}^\circ$	154	150	159	167	184	193
$\Delta H_{1,1,1}^\circ$	8.5 $\pm$ 1.3	6.4 $\pm$ 2.6	5.4 $\pm$ 0.6	12.9 $\pm$ 2.6	15.3 $\pm$ 2.3	14.7 $\pm$ 1.1
$\Delta G_{1,1,1}^\circ$	-30.59	-31.09	-31.92	-29.71	-29.33	-29.08
$\Delta S_{1,1,1}^\circ$	131	126	125	143	150	147
$\Delta H_{1,1,2}^\circ$	15.7 $\pm$ 2.5	16 $\pm$ 5	14.5 $\pm$ 1.5	20 $\pm$ 6	25.2 $\pm$ 3.8	26.6 $\pm$ 1.6
$\Delta G_{1,1,2}^\circ$	-43.7	43.6	-44.6	41.6	-41.1	-41.5
$\Delta S_{1,1,2}^\circ$	200	200	198	208	223	228
$\text{sig } Q_{\text{corr}}/\text{J}$	0.045	0.082	0.023	0.066	0.053	0.027
Number of points	58	57	48	58	57	59

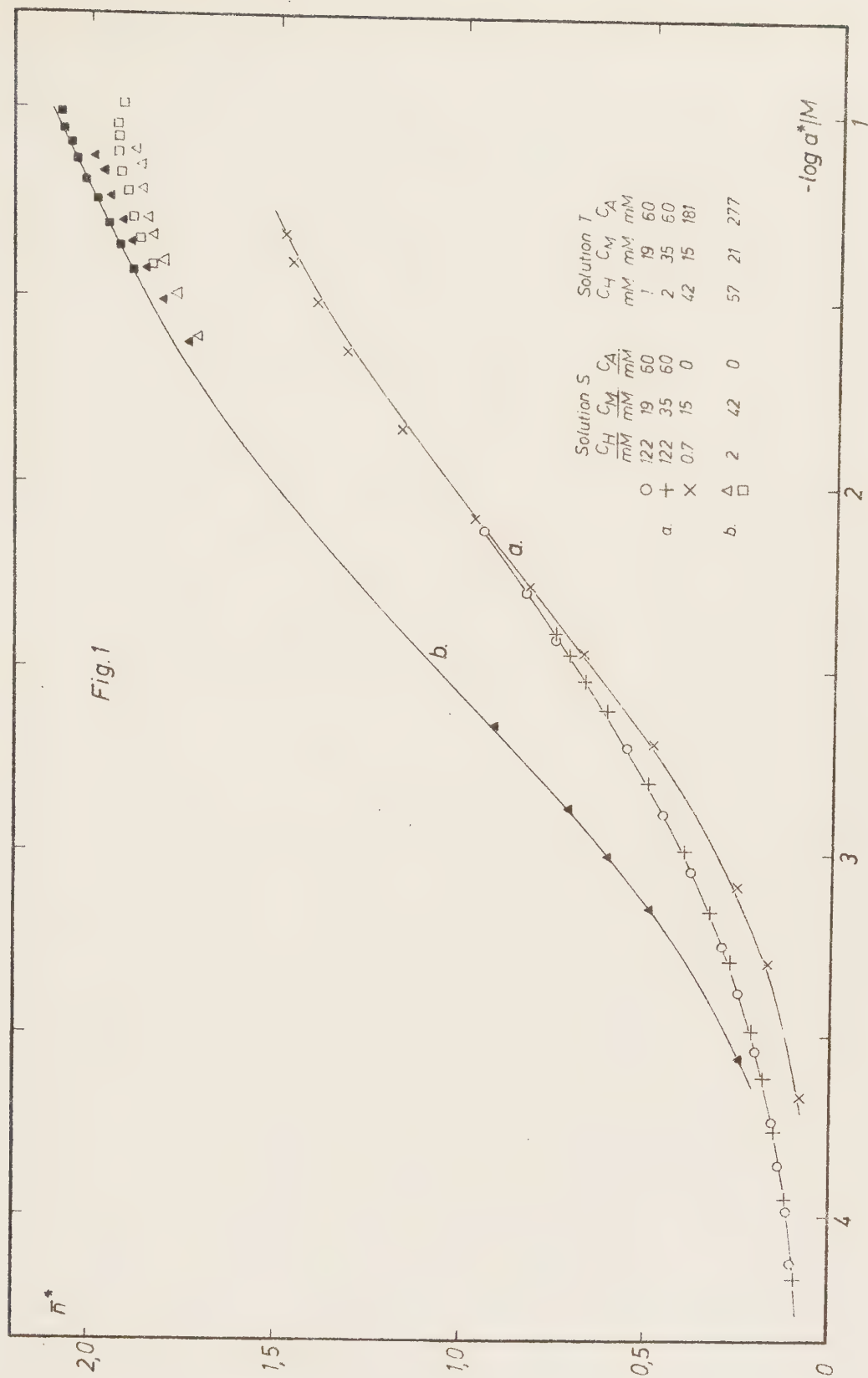
FIGURTEXT

Figure 1. Experimental $\bar{n}^*$ vs $-\log(\underline{a}^*/M)$ values for the praseodymium thiodiacetate system.

a. Results from the measurements in 1 M $\text{Na}(\text{ClO}_4)$. The curves have been calculated with the constants given in Table 3.

b. Results from the measurements in 4 M $\text{Na}(\text{ClO}_4)$. The curve is calculated with the constants given in Table 5. Values of $\bar{n}^*$ and $-\log \underline{a}^*/M$ have been calculated for two titration series with different values of the protonation constant $\beta_{0,1,1}$; viz.

Series 1 ($V_0 = 10$ ml)	$\beta_{0,1,1} = 3.93 \cdot 10^4/M$ (upper curve)
	$\beta_{0,1,1} = 3.74 \cdot 10^4/M$ (lower curve)
Series 2 ($V_0 = 20$ ml)	$\beta_{0,1,1} = 3.84 \cdot 10^4/M$ (upper curve)
	$\beta_{0,1,1} = 3.66 \cdot 10^4/M$ (lower curve)





Part IV.

Thermodynamic Properties of Rare Earth Complexes.

XIX. Free Energy, Enthalpy and Entropy Changes for the
Formation of Some Lanthanoid Maleate Complexes.

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The changes in free energy, enthalpy and entropy for the formation of Pr, Sm, Gd, Ho and Yb maleate complexes with the composition MA and MA₂ have been determined. The changes in free energy were calculated from stability constants, determined by a standard potentiometric method, viz. the determination of the concentration of free hydrogen ion, using a glass electrode. The enthalpy changes were measured calorimetrically. All data refer to a temperature of 25.0 °C and 1 M Na(ClO₄) medium.

A fairly small number of investigations of the complex formation of tervalent lanthanoids with bidentate ligands containing oxygen donors have been published. In most of these investigations only the stability constants have been determined, but in some cases, e.g. for the glycolate¹, malonate^{2,3}, kojate⁴, tropolonate⁵ and acetylacetonate⁶ systems, both free energy and enthalpy data for the complexation reactions have been obtained. The limited number of data is undoubtedly connected with the ease ^{of} formation of solid phases with this type of bidentate ligands.

Our series of investigations on lanthanoid dicarboxylate complexes has been extended to the maleate complexes in order to permit a further discussion of the following points:

a. We have been interested in the variation of thermodynamic quantities within the lanthanoid series. For the five ligands mentioned above, a regular and near linear variation of ΔG_i^0 , ΔH_i^0 and ΔS_i^0 with the ionic radius or the atomic number is found. This is at variance with the trends observed for a number of other ligands, e.g. oxydiacetate⁷ and imino-diacetate⁸, where $\Delta H^0(Z)$ and $\Delta S^0(Z)$ increase rapidly in the region Sr-Tb. As the malonate ion is the only dicarboxylate in the group of bidentate ligands ^{studied so far}⁹, it seems motivated to investigate the complexation reactions of another bidentate ligand, viz. the maleate ion.

b. When the ligand is the anion of a polyprotic acid, there is a possibility for the formation of acid complexes of the type MH_aA_r , $a > 0$. Such acid complexes have been detected, e.g. in the malonate and thio-diacetate¹⁰ systems. X-ray studies of solid maleic acid have shown that there is a strong intramolecular hydrogen bond in the hydrogen maleate ion¹¹. This bond must be broken when the hydrogen maleate ion forms a complex with a metal ion, thus rendering the formation of an acid complex

energetically unfavoured. Hence, the corresponding stability constants ought to be small. It is of interest to investigate whether this is true or not.

c. A well-established structural effect in chelate complexes is the enhanced stability of five-membered rings as compared to six-membered ones. The lanthanoid complexes with oxalate ion¹², which forms a five-membered ring, are much stronger than those formed with malonate ion⁹ where a six-membered ring is formed. We have been interested to see, if a further decrease in stability is observed when a chelate containing a seven-membered ring is formed. When this comparison is made, one has to be aware of the difference in ligand geometry of the maleate ion as compared to oxalate and malonate, due to the presence of a double bond in the maleate ion.

There are some earlier investigations on rare earth maleate complexes. Roulet et al.¹³ have determined stability constants for the 1:1 and 1:2 complexes at 25 °C and ionic strength 0.1 M (NaClO_4).

Paramonova et al.¹⁴ described the results of an ion-exchange study on the europium system by assuming that both maleate ion and hydrogen maleate ion formed 1:1 complexes with the metal ion.

No determinations of the enthalpy values of the complex formation reactions have been published for these systems.

This paper describes the determination of the changes in free energy, enthalpy and entropy for the formation of the Pr^{3+} , Sm^{3+} , Gd^{3+} , Ho^{3+} and Yb^{3+} maleates. The changes in free energy were calculated from the stability constants, which were determined from potentiometric measurements of the hydrogen ion concentration in solutions, containing metal perchlorate, maleic acid and disodium maleate. The enthalpy values were obtained in a direct calorimetric determination. The solvent was an

aqueous sodium perchlorate medium with the total sodium ion concentration equal to 1.00 M. The temperature was 25.0 ± 0.1 °C.

NOTATIONS AND CALCULATIONS

The notations have been defined earlier^{8,9}.

The stability constants and enthalpy values have been calculated by least-squares programs in the "Letagrop" series^{15,16}. Different error-carrying variables, viz. E/mV and $\bar{n}_H$, respectively, have been used in the calculation of the stability constants from $(v/ml, E/mV)$ -data. A least-squares program, using weighted $(a/M, \bar{n})$ -data has also been used¹⁷. The weighting scheme assumes that the relative error in the determination of the concentration of free ligand is constant.

In addition, standard graphical procedures have been used for some systems.

EXPERIMENTAL

Chemicals used. The preparation and standardisation of the lanthanoid perchlorate and sodium perchlorate solutions have been described earlier⁹.

The formula weight of the maleic acid (Fluka, p.a.) was determined by alcalimetric ^{titration} as 116.3 (calcd. 116.1). However, neither this method nor any electrometric titration with the equipment used here can be used to decide whether small amounts of fumaric acid are present or not. The presence of about 1 % fumaric acid ^{in the Fluka sample,} was shown by thin layer chromatography¹⁸. Maleic acid can be separated from fumaric acid by using the fact that only maleic acid can form an anhydride, which can be distilled¹⁹. Thus, a 0.5 M stock solution of maleic acid was prepared after distilling the

solid acid under reduced pressure, adding water to the anhydride obtained and standardising the solution with sodium hydroxide.

The potentiometric measurements on the proton and perchloric maleate systems were performed as titrations in the same way and with the same equipment as used before⁹. Contamination of the solutions with carbon-dioxide was prevented by bubbling nitrogen through the solution in the titration vessel. The experimental emf-values were corrected for a hydrogen ion and a perchlorate ion dependent liquid junction potential in the same way as was described for the malonates^{9,p.179}. The perchlorate ion dependent liquid junction potential amounts to 6.4 mV/l.

The stabilities of the proton maleate complexes were determined in solutions with $C_M = 0$ and with different constant values of the total maleate concentration, viz. $C_A = 25$ mM, 50 mM, 100 mM and 200 mM. With C_A -values greater than 125 mM, a precipitate with the composition $\text{NaHA} \cdot \frac{1}{2}\text{H}_2\text{O}$ (after air-drying) is formed in solutions with $\bar{n}_{\text{H}}$ approximately equal to 1.

In order to get precise values of the stability constants of the various complexes, a wide concentration range must be covered in the titrations. The ratio C_H/C_A varies from 1 to about 1/5, and the total metal ion concentration is in the range 15 mM to 40 mM. In solutions with $C_M > 20$ mM, a precipitate is formed when the value of $\bar{n}$ in the solution is close to 1.5.

The calorimetric measurements were made with the calorimeter developed by Grenthe, Ots and Ginstrup²⁰, using the same titrimetric technique as described for the malonates³.

The enthalpy values for the protonation of the maleate ion were determined by titrating disodium maleate solution with perchloric acid.

The heats of formation of the metal maleates were determined by titrating a metal solution with maleate buffers. The initial total metal ion concentration was about 20 mM, and two different buffer solutions with the ratio C_H/C_A equal to 2/5 and 1/3, respectively, were used. For each system, about 25 experimental points were measured.

RESULTS.

Determination of the stability constants.

The proton-maleate system. The potentiometric measurements were described by assuming the existence of two proton-maleate complexes, HA and H_2A , with the following stability constants:

$$\beta_{0,1,1} = (4.15 \pm 0.04) \cdot 10^5 \cdot M^{-1}$$

$$\beta_{0,2,1} = (1.65 \pm 0.03) \cdot 10^7 \cdot M^{-2}$$

These values were calculated in a "Letagrop" least-squares treatment of 182 experimental (v/ml , E/mV)-values. The standard deviation in C_H/C_A was equal to $6.3 \cdot 10^{-5}$. The experimental values are satisfactorily described by the calculated constants, except for some points with high $\bar{n}_H$ -values ($\bar{n}_H > 1.35$), where the values of $\bar{n}_{H,calc}$ exceed the $\bar{n}_{H,exp}$ -values with at most 1.5 percent. This deviation might in part be due to an error in the correction for the hydrogen ion dependent liquid junction potential in the very acid solutions used here.

The lanthanoid maleate systems.

Figure 1 shows calculated $\bar{n}$ vs. $-\log(a/M)$ curves for the samarium and ytterbium systems, together with some experimental points.

Primary data for the praseodymium system are given in Table 1, and the calculated stability constants for the systems investigated

are given in Table 2.

The stability constants have been calculated with the least-squares procedures using different error-carrying variables, viz. the measured emf $\underline{E}$ and $\underline{C}_H/\underline{C}_A$, respectively, in the "Letagrop" calculations. The same experimental points were used but the different choices of the error-carrying variable correspond to a different weighting of the data. The calculated values of the stability constants are the same in the two procedures, as they should be, but not the estimates of the corresponding standard deviations. Table 3 shows that the "Letagrop" procedure with the emf $\underline{E}$ as error-carrying variable gives the lowest values of the errors, especially for the stability constant $\underline{\beta}_{1,1,1}$ of the acid complex MHA. The largest estimates are obtained by using weighted $(\underline{a}/M, \underline{n})$ -data in the calculations. The limits of error for the constants, quoted in Table 2, have been calculated by multiplying these estimates of the standard deviations with three.

In the Pr, Sm and Gd systems measurements were made with solutions containing a high concentration of hydrogen maleate ion, in order to obtain information on the possible formation and the stability of an acid complex MHA. (These points have not been used for the calculations presented in Table 2). Table 3 shows that the calculated $\underline{\beta}_{1,1,1}$ -values are significantly positive for the praseodymium and gadolinium systems, though the estimated errors are fairly large. However, this fact is not sufficient to justify a claim as to the existence of this specie; the effects of experimental errors must also be considered. For the acid solutions used, small concentration errors or small errors in the measured emf give large errors in the constant $\underline{\beta}_{1,1,1}$. In fact, the positive values found for the Pr and Gd systems disappear if the total concentrations and $\underline{E}_O$ -values are changed in a few titration series with at most 0.5 % or 0.2 mV. The equilibrium constant $\underline{K}_{M,HA}$ for the reaction $M + HA \rightleftharpoons MHA$ is about 1 M^{-1} , according to the $\underline{\beta}_{1,1,1}$ -values found, and the experimental

technique used here thus gives an upper limit for $K_{M,MA}$ of about 2 M^{-1} . This is the value found by Paramonova et al.¹⁴ for the europium system in 0.5 M NaNO_3 .

The accuracy of the calculated stability constants depends on the uncertainties in the protonation constants; an error of 1 % in $\beta_{0,1,1}$ thus corresponds to an error of 1 % in $\beta_{1,0,1}$ and 3 % in $\beta_{1,0,2}$.

Determination of the enthalpy values.

The heats of protonation of the maleate ion were determined from 25 experimental points, and the following values were obtained:

$$\Delta H^{\circ}_{0,1,1} = (0.75 \pm 0.12) \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^{\circ}_{0,2,1} = (1.38 \pm 0.25) \text{ kJ} \cdot \text{mol}^{-1}$$

The standard deviation in Q_{corr} was 0.20 J. The errors are fairly large, but as this does not affect the further calculations on the metal complexes very much, no further work has been done on this system.

The values of the changes in free energy and entropy for the formation of proton-maleate complexes at 25°C are:

$$\Delta G^{\circ}_{0,1,1} = -32.14 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G^{\circ}_{0,2,1} = -40.69 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S^{\circ}_{0,1,1} = 110.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta S^{\circ}_{0,2,1} = 141.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Experimental data for the determination of the heats of formation of the praseodymium maleate complexes are given in Table 4. The Q_{corr} -values include the small correction for the heat capacity of the titrant. The overall enthalpy changes for the formation of the complexes are given in Table 5, together with the corresponding free energy and entropy changes. The standard deviation in the individual measurements, denoted $\text{sig } Q_{\text{corr}}$, is of the magnitude expected from the precision of the calorimetric equipment. The large error for

the praseodymium system is an exception which can not be explained, either as due to errors in the calorimetric procedure or to reasonable errors in the concentrations of the solutions.

DISCUSSION

The entropy of formation of lanthanoid maleate complexes is an approximately linear function of the atomic number, as is also the case for the malonates and other bidentate ligands with oxygen donors. The ΔH_1^0 -values are nearly the same for the malonates³ and the maleates; the small differences are, however, larger than the experimental errors.

The non-monotonous, "normal" variation pattern of thermodynamic properties across the lanthanoid series as shown by e.g. the oxydiacetates⁷, has been interpreted as due to a release of different numbers of water molecules in the complex formation reactions. This in turn might be a result of different hydration numbers for the lanthanoid ions. According to Choppin et al.⁴, the approximately linear behaviour of the ΔS^0 vs Z function is a reflection ^{of the fact,} that the mono-ligand complexes consist of species of different hydration in equilibrium. It is in principle possible to check this hypothesis, e.g. by measuring the temperature variation of ΔH^0 . This will be difficult to do experimentally with this type of ligand, as solid phases are easily formed. Measurements of this type on some malonate systems are, however, in progress at this laboratory.

In some cases, when the ligand is the anion of a polyprotic acid, protonated forms of the ligand also form complexes with lanthanoid ions. Stability constants $K_{M,HA}$ for the formation of some such ternary complexes are given in Table 6. The correlation between $K_{M,HA}$ and the protonation constant of the ligand HA is poor. According to experiments, the value of $K_{M,HA}$ is less than 2 M^{-1} for the maleates, i.e. hydrogen maleate ion forms the least stable complexes of the ligands quoted in Table 6. The formation of an acid maleate complex MHA with a chelated lanthanoid ion is energetically unfavoured, as a strong hydrogen bond in the hydrogen maleate ion has then to be broken. The large electrostatic repulsion from a chelated lanthanoid ion will also prevent a hydrogen ion from coordinating to any carboxylate oxygen.

The stability constants decrease in the order oxalates > malonates > maleates, i.e. the stability constants decrease when the size of the chelate ring increases. The enhanced stability of the malonates as compared to the maleates is almost entirely due to the more positive entropy change for the malonates. Nancollas et al.⁶¹ have calculated thermodynamic functions for the formation of oxalate and malonate complexes of some transition metal ions. The lower stabilities of the malonates was entirely an enthalpy effect. There are no determinations of enthalpy values for lanthanoid oxalate complexes, due to their low solubilities.

The effect on thermodynamic properties of changing the ionic medium can be assessed for the malonates and maleates, as complexes with both these ligands have been studied in different ionic media²². When the medium is changed from 0.1 M NaClO₄ to 1.00 M Na(ClO₄), there is a change in the ΔG_1^0 -values with about + 5 kJ·mol⁻¹, both for the malonates and maleates¹³. This is mainly due to a corresponding decrease in ΔS_1^0 , whereas the enthalpy changes, ΔH_1^0 , are less sensitive to changes in the ionic medium.

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Table 1. Experimental results of the potentiometric measurements on the praseodymium maleate system. Values of $\underline{V}$ /ml and $\underline{E}$ /mV are given. The sodium ion concentration is 1.00 M in all solutions.

Series 1. S: $\underline{C}_H = 0.00091$ M, $\underline{C}_M = 0.01941$ M, $\underline{C}_A = 0$;

T: $\underline{C}_H = 0.06254$ M, $\underline{C}_M = 0.01941$ M, $\underline{C}_A = 0.1807$ M;

$\underline{V}_O = 19.96$ ml; $\underline{E}_O = 497.7$ mV.

0.250, 253.8; 0.500, 233.4; 0.750, 226.0; 1.000, 221.5;

1.500, 215.8; 2.000, 211.5; 3.000, 205.2; 4.000, 200.1

5.000, 195.4; 7.000, 187.7; 9.000, 182.3; 12.00, 176.7;

Series 2. S: $\underline{C}_H = 0.00148$ M, $\underline{C}_M = 0.03115$ M, $\underline{C}_A = 0$;

T: $\underline{C}_H = 0.08322$ M, $\underline{C}_M = 0.03115$ M, $\underline{C}_A = 0.1908$ M;

$\underline{V}_O = 19.96$ ml; $\underline{E}_O = 497.3$ mV.

0.500, 265.0; 0.750, 254.0; 1.000, 248.6; 1.500, 242.1;

2.000, 238.3; 2.500, 235.2; 3.000, 233.3; 4.000, 229.7;

5.000, 226.9; 7.000, 221.5; 10.00, 214.6; 12.00, 210.7;

15.00, 205.7; 17.00, 203.0;

Series 3. S: $\underline{C}_H = 0.05072$ M, $\underline{C}_M = 0.02009$ M, $\underline{C}_A = 0.02500$ M;

T: $\underline{C}_H = 0.00081$ M, $\underline{C}_M = 0.02009$ M, $\underline{C}_A = 0.02500$ M;

$\underline{V}_O = 20.01$ ml; $\underline{E}_O = 389.5$ mV.

3.000, 275.2; 5.000, 269.3; 7.000, 263.3; 9.000, 257.1;

11.00, 250.5; 14.00, 239.5; 17.00, 226.1; 20.00, 208.8;

25.00, 178.8; 30.00, 159.9;

Series 4. S: $\underline{C}_H = 0.02078 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.02500 \text{ M}$;
T: $\underline{C}_H = 0.00081 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.02500 \text{ M}$;
 $\underline{V}_O = 30.00 \text{ ml}$; $\underline{E}_O = 389.3 \text{ mV}$.
5.000, 140.8; 10.00, 122.1; 15.00, 120.4; 20.00, 113.9;
25.00, 108.5; 30.00, 103.7;

Series 5. S: $\underline{C}_H = 0.0108 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.02500 \text{ M}$;
T: $\underline{C}_H = 0.00081 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.02500 \text{ M}$;
 $\underline{V}_O = 20.01 \text{ ml}$; $\underline{E}_O = 389.3 \text{ mV}$.
5.000, 93.1; 10.00, 85.7; 15.00, 79.8; 20.00, 75.2;

Series 6. S: $\underline{C}_H = 0.00581 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.02500 \text{ M}$;
T: $\underline{C}_H = 0.00081 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.02500 \text{ M}$;
 $\underline{V}_O = 20.00 \text{ ml}$; $\underline{E}_O = 389.2 \text{ mV}$.
5.000, 68.1; 10.00, 63.0;

Series 7. S: $\underline{C}_H = 0.1007 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.05000 \text{ M}$;
T: $\underline{C}_H = 0.00090 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.05000 \text{ M}$;
 $\underline{V}_O = 20.01 \text{ ml}$; $\underline{E}_O = 389.4 \text{ mV}$.
5.000, 279.3; 7.000, 272.4; 9.000, 265.4; 11.00, 258.2;
14.00, 245.8; 17.00, 230.4; 20.00, 209.7; 25.00, 174.2;
30.00, 153.2;

Series 8. S: $\underline{C}_H = 0.04083 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.05000 \text{ M}$;
T: $\underline{C}_H = 0.00090 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.05000 \text{ M}$;
 $\underline{V}_O = 30.00 \text{ ml}$; $\underline{E}_O = 389.0 \text{ mV}$.
5.000, 131.7; 10.00, 117.8; 15.00, 107.5; 20.00, 99.4;
25.00, 92.8; 30.00, 87.3;

Series 9. S: $\underline{C}_H = 0.02087 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.05000 \text{ M}$;

T: $\underline{C}_H = 0.00090 \text{ M}$, $\underline{C}_M = 0.02009 \text{ M}$, $\underline{C}_A = 0.05000 \text{ M}$;

$\underline{V}_O = 20.00 \text{ ml}$; $\underline{E}_O = 388.9 \text{ mV}$.

5.000, 75.0; 10.00, 66.4; 15.00, 59.9; 20.00, 54.7.

Table 2. The overall stability constants for the malate comp. . . ,
calculated from $([A], \bar{n})$ -data. The errors are equal to three standard
deviations.

Metal ion	Number of experimental points	$\beta_{1,0,1} \cdot 10^{-2} \cdot M$	$\beta_{1,0,2} \cdot 10^{-4} \cdot M^{-2}$
Pr	56	6.50 ± 0.22	4.96 ± 0.16
Sm	143	9.98 ± 0.09	8.00 ± 0.15
Gd	73	9.24 ± 0.10	6.10 ± 0.14
Ho	59	7.73 ± 0.34	4.73 ± 0.50
Yb	60	6.39 ± 0.13	4.44 ± 0.18

Table 3. "Letagrop" calculations of the stability constants for the Pr, Sm and Gd maleate complexes with different error-carrying variable $\underline{y}$, and with two different assumptions as to which complexes are formed. The number of experimental points is also given.

		$\underline{y} = \frac{C_H}{C_A}$		$\underline{y} = E$	
Metal ion	Assumed complexes	$\text{sig } \underline{y} \cdot 10^3$	Calculated stability constants	$\text{sig } \underline{y}/\text{mV}$	Calculated stability constants
Pr (67 p).	MA	3.81	$(6.22 \pm 0.10) \cdot 10^2$	0.44	$(6.27 \pm 0.10) \cdot 10^2$
	MA ₂		$(5.05 \pm 0.21) \cdot 10^4$		$(5.01 \pm 0.17) \cdot 10^4$
	MA	3.33	$(6.42 \pm 0.16) \cdot 10^2$	0.45	$(6.36 \pm 0.10) \cdot 10^2$
	MA ₂		$5.1 \cdot 10^4$		$5.1 \cdot 10^4$
	MHA		$(3.9 \pm 2.9) \cdot 10^5$		$(1.75 \pm 0.80) \cdot 10^5$
Sm (239 p).	MA	3.62	$(10.02 \pm 0.08) \cdot 10^2$	0.64	$(10.28 \pm 0.08) \cdot 10^2$
	MA ₂		$(8.09 \pm 0.20) \cdot 10^4$		$(8.27 \pm 0.17) \cdot 10^4$
	MA	4.33	$(10.09 \pm 0.09) \cdot 10^2$		The calculations did not converge.
	MA ₂		$8.1 \cdot 10^4$		
	MHA		$(0 \pm 2.4) \cdot 10^5$		
Gd (132 p).	MA	2.67	$(9.14 \pm 0.09) \cdot 10^2$	0.41	$(9.02 \pm 0.04) \cdot 10^2$
	MA ₂		$(5.97 \pm 0.13) \cdot 10^4$		$(6.00 \pm 0.01) \cdot 10^4$
	MA	2.43	$(9.31 \pm 0.12) \cdot 10^2$	0.37	$(9.17 \pm 0.09) \cdot 10^2$
	MA ₂		$6.0 \cdot 10^4$		$6.0 \cdot 10^4$
	MHA		$(2.5 \pm 1.3) \cdot 10^5$		$(1.3 \pm 0.14) \cdot 10^5$

Series 4a. S: $\underline{C}_H = 0.000436 \text{ M}$, $\underline{C}_M = 0.01837 \text{ M}$, $\underline{C}_A = 0$;

T: $\underline{C}_H = 0.1032 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.3011 \text{ M}$;

$\underline{V}_O = 79.93 \text{ ml.}$

2.000, 3.410, 0.117; 5.000, 5.192, 0.021; 8.000, 4.481, -0.167;

11.00, 3.431, -0.151; 14.00, 2.393, -0.033; 17.00, 1.573, 0.088;

20.00, 1.063, 0.113;

Series 4b. S: $\underline{C}_H = 0.02100 \text{ M}$, $\underline{C}_M = 0.01469 \text{ M}$, $\underline{C}_A = 0.06027 \text{ M}$;

T: $\underline{C}_H = 0.1032 \text{ M}$, $\underline{C}_M = 0$, $\underline{C}_A = 0.3011 \text{ M}$;

$\underline{V}_O = 84.93 \text{ ml.}$

3.000, 0.628, 0.201; 6.000, 0.519, 0.063; 9.000, 0.347, 0.079;

Table 5. The changes in enthalpy, free energy and entropy for the formation of lanthanoid maleate complexes.

The errors in the enthalpy values are equal to three standard deviations.

Metal ion	Standard deviation in Q_{corr}/J	$\frac{\Delta H_{1,0,1}^{\circ}}{kJ \cdot mol^{-1}}$	$\frac{\Delta G_{1,0,1}^{\circ}}{kJ \cdot mol^{-1}}$	$\frac{\Delta S_{1,0,1}^{\circ}}{J \cdot mol^{-1} K^{-1}}$	$\frac{\Delta H_{1,0,2}^{\circ}}{kJ \cdot mol^{-1}}$	$\frac{\Delta G_{1,0,2}^{\circ}}{kJ \cdot mol^{-1}}$	$\frac{\Delta S_{1,0,2}^{\circ}}{J \cdot mol^{-1} K^{-1}}$
Pr	0.116	10.80±0.45	-15.99	89.8	20.0±0.8	-26.90	157
Sm	0.044	10.67±0.13	-17.22	93.5	17.74±0.23	-28.08	153
Gd	0.043	12.51±0.12	-16.94	98.8	19.83±0.23	-27.36	158
Ho	0.076	15.44±0.23	-16.47	107.0	24.1±0.5	-26.60	170
Yb	0.055	16.32±0.16	-16.07	108.6	27.03±0.29	-26.47	179

Table 6. The protonation constants ($K_{H,HA}$) and stability constants for europium (or samarium) complexes ($K_{M,HA}$) with some protonated ligands.

		Ligand:						
		hydrogen oxalate ion	hydrogen maleate ion	imino- diacetic acid	hydrogen malonate ion	hydrogen iminodi- acetate ion	hydrogen thiodi- acetate ion	hydrogen succinate ion
$\log(K_{H,HA} \cdot M)$	0.91	1.53	1.60	1.88	2.55	2.58	3.13	4.2
$\log(K_{M,HA} \cdot M)$	1.50 (M=Eu ³⁺)	0.3 (M=Eu ³⁺)	<0.3	0.97 (M=Eu ³⁺)	1.42 (M=Eu ³⁺)	1.48 (M=Eu ³⁺)	1.60 (M=Sm ³⁺)	2.0 (M=Eu ³⁺)
Reference	14	14	This study	8	9	8	10	25

FIGURTEXT

Figure 1. Experimental $\bar{n}$ vs $-\log(a/M)$ data for the samarium and ytterbium systems. The curves have been calculated with the constants in Table 2. The value of b is zero for the Sm system and 0.25 for the Yb system. Titrations with $C_M = 20$ mM and 40 mM are denoted with o and +, respectively.

